LIGHT-SCATTERING STUDIES

ON THE

POLYMER AND POLYELECTROLYTE

FROM

2 - VINYL PYRIDINE

BY

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SUMMARY.

Part 1.

Several batches of 2-vinyl pyridine are polymerised using azo-bis-isobutyronitrile as initiator. The polymer obtained is fractionated by a precipitation method using benzene as solvent and n-hexane as precipitant. Viscosity and light-scattering measurements are made on ten fractions. The solvents are ethanol and a θ-solvent, the composition of which, is determined as n-propanol (volume fraction 0.365) and n-heptane (volume fraction 0.635) at 25°C by precipitation measurements.

Light-scattering measurements indicate that the mixed solvent used is slightly better than ideal. Molecular weights and dimensions together with second virial coefficients and limiting viscosity numbers are reported for the polymer in the two solvents. The molecular dimensions corresponding to those in a true θ-solvent are obtained by extrapolation of the measured data.

The equations relating the solution properties of this polymer to the molecular weight are shown below :-

Viscosity - Molecular Weight :-

Ethanol $[\eta] = 2.8 \times 10^{-4} M_w^{0.66}$

Mixed Solvent $[\eta] = 1.2 \times 10^{-3} M_w^{0.50}$

Molecular Dimensions - Molecular Weight :-

Ethanol $\langle R^2 \rangle_z = 0.063\ M_w^{1.25}$

Mixed Solvent $\langle R^2 \rangle_z = 0.49\ M_w^{1.08}$

True θ-solvent $\langle R^2 \rangle_z = 1.1\ M_w^{1.00}$

Second Virial Coefficient :-

Ethanol $B = 2.5 \times 10^{-3}\ M^{-0.41}$

ν in the general equation :-

$$\langle R^2 \rangle = KM^{1+\nu}$$

is calculated by different methods from measurements in ethanol. The values obtained are not self-consistent.

The term $\overline{\cos\phi}$ in the equation :-

$$\langle R^2 \rangle = n\,l^2\,\frac{1-\cos\theta}{1+\cos\theta}\cdot\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}}$$

is calculated for three different solvents taking into account excluded volume. The values of $\overline{\cos\phi}$ increase as the solvent becomes better indicating that there is less hindrance to rotation in the polymer chain at more extended configurations. Tests of current equations relating α, the Flory expansion factor, to molecular weight are made. The agreement, in accordance with that obtained by other workers, is poor.

Part 2.

Two fractions of poly-2-vinyl pyridine are converted to polyelectrolyte by a quaternisation reaction with n-propyl bromide. While the reaction is incomplete ca. 70 %, the products exhibit the solution properties of highly charged synthetic polyelectrolytes.

Light-scattering experiments, using liquids of high dielectric constant as solvent e.g. dimethyl sulphoxide and water, reveal unusual light-scattering behaviour including inconsistent molecular weights and variation in the angular dependence of scattered light with concentration leading to incorrect values of molecular dimensions. These effects are interpreted as being due to long range electrostatic forces existing in the solution even at very low concentration which alter both the intensity of light scattered and its angular distribution.

Experiments made using aqueous solutions of potassium bromide as solvent corroborate the findings in the pure liquids. At high ionic strength the interactions are suppressed but at low ionic strength of solution interpretation of data is difficult due to the distortion of light-scattering by these interactions. By using very low concentrations of polyelectrolyte ($0.5 - 2.0 \times 10^{-4}$ gm/ml.) reliable dimensions for the molecules are obtained over a range in ionic strength from 0.4 - 0.01

The effect of large intermolecular forces in solution on its light-scattering is verified by measurements using high concentrations of uncharged, high molecular weight polymer. The shape of the reciprocal intensity scattering

envelope is discussed.

The variation of molecular dimensions of the high molecular weight sample of polyelectrolyte is examined quantitatively using the theory of Rice and Harris. Good agreement is obtained between the calculated values and those obtained from light-scattering over a range in ionic strength from 0.01 to 0.4

It is concluded that, for reliance to be placed on measurements of molecular weights and dimensions of charged polymers obtained by light-scattering, the concentration of simple electrolyte must be great enough to eliminate large molecular interactions. This sets a lower limit to the range of ionic strength over which polyelectrolyte dimensions may be studied by light-scattering techniques.

FORM OF THESIS

The thesis has been presented in two parts :-

Part 1 includes some fundamental theory of polymer solutions and of light-scattering together with results obtained in experiments made on poly-2-vinyl pyridine which are discussed in the light of current knowledge in the field of polymer solutions.

Part 2 comprises the results and discussion of an investigation of the unique light-scattering behaviour observed for poly-2-vinyl n-propyl pyridinium bromide in several solvents.

PART 1.

INTRODUCTION

Thomas Graham[1] in 1861 coined the term "colloids" to describe various substances which showed negligible rates of diffusion in solution and which did not pass through semipermeable membranes. Other species which showed the then more normal solution properties and which could be obtained in a crystalline form he termed "crystalloids".

For many years there was much discussion over the type of bonding in colloids and it emerged that there were two types of colloids. Some could be prepared from almost any material and might be reconverted, by purely physical treatment, to a crystalline form. Others could only be obtained in a colloidal state and the bonding was described in terms of "partial valencies".

It was not until 1920 that Staudinger[2] proposed chain structures for many of the polymeric substances such as polystyrene, polyoxymethylene and natural rubber. He defined the high polymeric substances as macromolecules which exhibit colloidal properties in all solvents in which they dissolve whereas the association colloids may lose their colloidal character in some solvents.

One reason for lack of acceptance of the chain hypothesis was the non-uniformity in the chain length so that a precise chemical species could not be defined. Staudinger also introduced the idea of non-linear polymers which we now describe as branched.

In 1930 Kuhn[3] applied statistical methods to the degradation of cellulose assuming random splitting of bonds. Since a polymer as depicted by Staudinger furnished an ideal

case for the methods of statistics, theoretical investigations of the average size and shape of long chain molecules were made by Guth and Mark[4], Kuhn[5] and Eyring[6].

A direct proportionality between the limiting viscosity number, then called intrinsic viscosity, and the molecular weight was proposed by Staudinger[7] and although this is no longer accepted it was an important step in indicating a relationship between these two quantities.

A major drawback to advancement in the field of polymer study was the lack of precise experimental methods since the usual methods of molecular weight estimation e.g. ebulliometry cryoscopy and osmometry proved rather inaccurate for the very large molecular weights encountered in polymeric materials.

In the early investigations osmometry was used to determine the molecular weights employed in the Mark-Houwink[8,9] equation relating viscosity and molecular weight. Osmometry gives the number average molecular weight and while information about polymer solvent interactions could be obtained no information could be derived concerning the dimensions of the polymer in solution

The advent of light scattering techniques occurred in the 1940's when several papers were published concerning the theory and application of light scattering to polymer solutions. In 1944 Doty, Zimm and Mark[10] described how molecular weights and osmotic second virial coefficients could be determined by light scattering and in 1948 Zimm[11,12] published his two classical papers on the subject. The first dealt with the expression for the reciprocal intensity

surface of scattered light and with the methods of extrapolation, while the second described the apparatus and results which could be obtained. In 1950, Outer, Carr and Zimm[13] published a very comprehensive account of an investigation of light scattering of polystyrene in various solvents. Also in 1950 Doty and Steiner[14] published their compilation of scattering functions from which the shape and size of particles could be deduced using experimental results.

In the same period theories of polymer solutions were being evolved from a thermodynamic and hydrodynamic stand-point. The earliest theory of Flory and Huggins[15] was followed by those of Debye and Bueche[16] and Kirkwood and Riseman[17] and later in 1951 by that of Flory and Fox[18]. These theories dealt with the viscosity of polymer solutions from a theoretical viewpoint and with the interactions and dimensions deduced from statistical thermodynamic reasoning.

Statistical methods were also applied to polymer molecules in order to determine the molecular dimensions in terms of bond length, bond angle, freedom of rotation about bonds and degree of polymerisation. Equivalent equations were independently deduced by Kuhn[19], Taylor[20] and Benoit[21]. This expression applies to molecules having a purely random configuration and does not apply in many solvents where the polymer coil is expanded by interaction with the solvent. Because of this effect a further modification of thought concerning polymer dimensions was made. The increase in size over that expected on the random coil model has been termed the excluded volume effect and has been the subject of many theoretical papers. The subject has been treated in

several different aspects by many authors[22-29]. Zimm, Flory, Fixman, Albrecht, Stockmayer and Fisher have all published results on the subject and the question is by no means completely resolved.

The thermodynamic theories of polymer solutions have been employed to describe phase equilibria in such solutions and experimental results have been quoted for several systems by Schultz[30].

In addition to the large number of experimental publications which have appeared since that of Zimm in 1950 covering a wide range of polymers and solvents, many additions to the fundamental theory have been made. Benoit[31] has described methods of obtaining number average molecular weights from light scattering. Peterlin[32] has indicated scattering functions for stiffened coils which find application in the study of large naturally occurring molecules. The equations of light scattering have been extended to multicomponent systems notably by Kirkwood and Goldberg[33] and Stockmayer[34]. These equations are of greatest use in the studies of proteins in the presence of added electrolyte.

While there remain many discrepancies between theory and experiment in the field of polymer solutions, such as excluded volume and polymer polymer interactions, for very dilute solutions great advances have been made since Staudinger proposed the chain structure and the nature of macromolecules in solution now seems to be fairly well understood.

Nomenclature.

For convenience of notation a list is given below of the principal symbols used in the field of polymer solutions with their meaning.

M_n, M_w, M_z - The number, weight and "z" average molecular weights. These are defined by

$$M_n = \frac{\sum c_i}{\sum \frac{c_i}{M_i}} = \frac{\sum m_i M_i}{\sum m_i}$$

$$M_w = \frac{\sum c_i M_i}{\sum c_i} = \frac{\sum m_i M_i^2}{\sum m_i M_i}$$

$$M_z = \frac{\sum c_i M_i^2}{\sum c_i M_i} = \frac{\sum m_i M_i^3}{\sum m_i M_i^2}$$

where M_i is the molecular weight of the species "i" having a weight concentration c_i and molar concentration m_i.

$\langle R^2 \rangle_n$, $\langle R^2 \rangle_w$, $\langle R^2 \rangle_z$ - The number, weight and "z" averages of the mean square of the distance between the ends of a polymer chain.

The subscript "o" as in "$\langle R_o^2 \rangle_z$", indicates the quantity obtained for a polymer molecule behaving as a typical random coil.

$\langle \rho^2 \rangle_n, \langle \rho^2 \rangle_w, \langle \rho^2 \rangle_z$ — The number, weight and "z" averages of the mean square of the polar radius of gyration of any particle.

$[\eta]$ — This quantity is now termed the limiting viscosity number and was formerly referred to as the intrinsic viscosity.

B — The second virial coefficient for a polymer in a solvent and may be thought of either as a measure of solute-solvent interactions or solute-solute interactions.

n — The number of bonds in a polymer chain.

Θ — 1. The valence angle.
2. The angle between the incident beam and the scattered beam.

ϕ — The angle which any bond in a polymer chain makes with the plane of the two preceding bonds.

I or i — Intensity of incident or scattered light.

Average values are sometimes, for convenience, denoted by a bar above the symbol i.e. $\overline{\rho^2}$ is identical to $\langle \rho^2 \rangle$.

Configuration of Polymer Chains.

As detailed above the expression for the mean square end to end distance of a polymer chain was derived by Kuhn, Taylor and Benoit. Because of their importance in understanding the nature of a polymer in solution the effects acting on a polymer molecule are described briefly below.

In Kuhn's calculations he assumes statistical elements which are freely jointed. These "statistical elements" may consist of a number of bonds such that the total number of statistical elements is still large but that the angle between any one element and that preceding it is completely random. From this model the relation between $\langle R^2 \rangle$ and n' the number of statistical elements is

$$\langle R_o^2 \rangle = l'^2 (n') \quad \ldots\ldots\ldots\ldots (1)$$

where l' is the length of a particular element.

Similarly if we assume a model where l' becomes l the bond length and n the number of bonds in the chain the expression would be

$$\langle R_o^2 \rangle = l^2 n \quad \ldots\ldots\ldots\ldots\ldots (2)$$

This treatment is not valid since the angle between any bond and that preceding it is not random but is determined by valency angles and limited freedom of rotation of one bond about another.

Influence of Valence Angle.

To take account of a fixed valence angle in a carbon chain it is assumed that any bond can rotate freely about the preceding bond keeping the valence angle fixed.

If θ is the valence angle it can be shown that[35]

$$\langle R_o^2 \rangle = nl^2 \left\{ \frac{1-\cos\theta}{1+\cos\theta} + \left(\frac{2\cos\theta}{n} \right) \left[\frac{1-(-\cos\theta)^n}{(1+\cos\theta)^2} \right] \right\} \quad \ldots\ldots(3)$$

from which it can be seen that when n is large as it is for most polymers the above equation reduces to

$$\langle R_o^2 \rangle = nl^2 \left(\frac{1-\cos\theta}{1+\cos\theta} \right) \quad \ldots\ldots(4)$$

Hindrance to Rotation.

The above picture may be a fairly good approximation for a chain such as that of polymethylene where freedom of rotation may be expected. In many polymer chains however there are large side groups on the chain such as the phenyl groups in polystyrene. These will tend to prevent free rotation and as a result will cause the chain to take up a more expanded configuration. The angle ϕ is used as the quantity to define this hindrance to rotation and by an analysis similar to that above, the expression for $\langle R_o^2 \rangle$ may be written as

$$R_o^2 = nl^2 \left(\frac{1-\cos\theta}{1+\cos\theta} \right) \left(\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}} \right) \quad \ldots\ldots(5)$$

where $\overline{\cos\phi}$ is the average value of $\cos\phi$. This equation

applies when $\overline{\cos\phi}$ is not close to unity and reduces to that for a freely rotating chain when $\overline{\cos\phi}$ is zero.

These models and treatments are accurate when there is direct proportionality between $\langle R_o^2 \rangle$ and n. This occurs in the special case of an "ideal" solvent. It is seen that the third and fourth terms in the above equation are constants and are independent of n. For this reason they have been termed short range or "skeletal" effects.

On consideration of the problem of applying random walk statistics to a connected chain of bonds a severe limitation is immediately observed, namely that since the chain segments have a finite thickness they cannot interpenetrate or even approach to very close range. Because of this, more expanded configurations are favoured since these tend to reduce interactions between widely separated segments of the same molecule.

One of the most useful methods of describing the larger sizes of molecules in good solvents than those predicted in the above expressions has been by Flory and Fox. In their treatment of this subject an expansion factor α is defined such that

$$\langle R^2 \rangle = \alpha^2 \langle R_o^2 \rangle \quad \ldots\ldots\ldots\ldots (6)$$

where $\langle R_o^2 \rangle$ is the mean square end to end distance described in the above formulae. It is evident that as the number of segments in the chain increases, the more the configuration will be extended. This may be described by an equation of the form

$$\langle R^2 \rangle = KM^{1+\nu} \quad \ldots\ldots\ldots\ldots (7)$$

where ν is usually a small positive number and K is a constant. This effect of excluded volume in addition to being connected with the number of segments in the chain is also allied to the interactions between molecules in solution.

An analogy may be made to the interactions in a gas comprising attractive forces and repulsive forces due to volume exclusion. One fundamental difference is apparent however, namely that while by reducing the pressure of a gas, intermolecular forces may be reduced to zero, in a polymer solution even at infinite dilution intramolecular interactions will still exist.

The term α in the above equation incorporates both the physical volume from which one polymer segment excludes another and the forces of attraction which are governed by the nature of the solvent. In some solvents the attractive forces just compensate the repulsive effect of excluded volume and the molecule can exist in a purely random configuration. This is apparent in the Flory-Fox Theory where such a solvent is defined as a "theta" solvent or the system as being at a "theta" temperature.

The above discussion concerns the state of affairs in infinitely dilute solution. The effect of concentration on the solution is dealt with in the virial expansion for the various solution properties e.g. $\frac{\pi}{c}$ for the osmotic pressure and $\frac{Kc}{R_\theta}$ for light scattering. Outer, Carr and Zimm have shown that in good solvents with large solvent

interactions B, the second term in this series will be large due to the molecule being swollen whereas when these polymer-solvent interactions are small the value of B decreases and in the limit of B equal to zero the attractive forces are counterbalanced by the repulsion due to excluded volume. The connection between excluded volume and the second virial coefficient is complex and due to mathematical difficulty has not been completely resolved.

Stockmayer has evaluated α^2 in terms of a series expansion and expressions have also been deduced relating the second virial coefficient to α^2 [36,37,38].

The difficulties associated with this aspect of chain configuration may be summarised as the difficulty in relating the excluded volume quantitatively to α and also to that of finding suitable experimentally accessible thermodynamic parameters to characterise the interactions between polymer segments and solvent.

Hydrodynamic Theories of Polymer Solutions.

To determine the dependence of the viscosity of polymer solutions on molecular chain length and dimensions three models have been treated hydrodynamically.

1. The Free Draining Model :-

This assumes that the resistance of a polymer coil to the flow of solvent is related only to the number of segments in the chain and that the molecule as a whole is completely permeable to the solvent.

The molecule is likened to a "string of beads" and Stoke's Law is applied to each bead

$$\zeta = 6\pi\eta_0 a \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where ζ is the frictional coefficient for a bead, η_0 is the viscosity of the solvent and a the radius of a bead.

Considering translational and rotational motion of the polymer molecule in a solvent the expression for the limiting viscosity number in absence of intramolecular interactions is given by

$$[\eta] = \frac{\zeta N_A}{\eta_0 M_0} \frac{\overline{\rho^2}}{400} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

where M_0 is the molecular weight of a bead and $\overline{\rho^2}$ the mean square radius of gyration of the molecule. Since $\overline{\rho^2} \propto a^2 M$ where M is the molecular weoght of the polymer, $[\eta]$ should increase as a power of M higher than the first.

2. Equivalent Sphere Model :-

In a real polymer molecule it seems unlikely that all parts of the coil will be completely permeable to the solvent. This may be true of the outer fringes of the molecule, but nearer the centre the solvent will begin to behave more and more as though it were attached to the segments. This introduces the idea that the molecule as a whole can be represented by an equivalent sphere which is impenetrable to the solvent.

If R_e is the radius of this sphere we obtain

$$[\eta] = \frac{0.025 N_A V_e}{M} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Intuitively it has been suggested that R_e is proportional to the root mean square radius of gyration of the molecule so that

$$[\eta] = K\alpha^3 M^{\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Although this equation has been verified by most experimental studies the reasoning leading to it is not at all rigorous.

3. Real Polymer Chains[39] :-

A real polymer chain is thought to behave as a combination of the two models described above. The molecular friction coefficient $\frac{f_o}{\eta_o}$ may be written as

$$\frac{f_o}{\eta_o} = \langle \rho^2 \rangle^{\frac{1}{2}} \phi\left(\frac{\varepsilon}{\eta_o}, x, \langle \rho^2 \rangle^{\frac{1}{2}}\right)$$

where x is the number of segments in the chain and ϕ is a function of the variables shown which reaches an upper limit as x increases. It can be shown by dimensional analysis that

$$\frac{f_o}{\eta_o} = \langle \rho^2 \rangle^{\frac{1}{2}} \phi\left[x \frac{\zeta}{\eta_o} \langle \rho^2 \rangle^{\frac{1}{2}}\right]$$

$\frac{f_o}{\eta_o} = P' \langle \rho^2 \rangle^{\frac{1}{2}}$ where P' is the limiting value of ϕ at large values of x. Applying the Kirkwood-Riseman Theory the expression for the limiting viscosity number is

$$[\eta] = \left(\frac{\pi}{6}\right)^{3/2} \left(\frac{N_A}{100}\right) XF(X) \frac{\langle R^2 \rangle^{3/2}}{M} \quad \ldots\ldots\ldots(12)$$

where $X = (6\pi^3)^{-\frac{1}{2}} \times \frac{\zeta}{\eta_o} \langle R^2 \rangle^{1/2}$ and F(X) is a function of X.

For large values of x, XF(X) reaches an asymptotic limit of 1.588.

Thus

$$[\eta] = \Phi \frac{\langle R^2 \rangle^{3/2}}{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

where Φ has the value 3.62×10^{21}

From these considerations Φ should be independent of the nature of the polymer and solvent. In most experimental determinations of Φ for various systems values of $2.0 - 2.5 \times 10^{21}$ are obtained. The reason for the discrepancy is not clear but the constancy in the

experimental value of $\underline{\Phi}$ indicates that some modification of the theory is required.

Incorporating the expansion factor α into the last equation

$$[\eta] = \underline{\Phi}\left(\frac{\langle R_o^2 \rangle}{M}\right)^{3/2} M^{\frac{1}{2}}\alpha^3 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

and combining this with the semi-empirical equation $[\eta] = KM^{\frac{1}{2}}\alpha^3$ we obtain

$$K = \underline{\Phi}\left(\frac{\langle R_o^2 \rangle}{M}\right)^{3/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(15)$$

Thus the K in the viscosity molecular weight equation should be a constant which is independent of molecular weight and solvent but which, since $\langle R_o^2 \rangle$ may change with temperature, should alter with temperature.

Theory of Light-Scattering.

The effect of light-scattering has been known for many years. In 1802 Richter[40] observed scattering from colloidal gold. Tyndall[41] investigated the effect and found that the direction of the scattered light was dependent on the polarisation of the incident beam. Lord Rayleigh in 1871[42] treated the phenomenon as one of diffraction which he found to be very dependent on the wavelength of the incident light.

Qualitatively the process may be explained as that in which a beam of light passing through a medium sets up oscillating electric moments in the particles. These act as secondary sources of radiation which has the same wavelength as the incident radiation. This is the scattered light. A small proportion of the absorbed radiation is used to raise the molecules to higher energy states. This is re-emitted in radiation of different wavelength as Raman spectra. The intensity of this radiation is negligible compared to that of the scattered light and is usually neglected.

The early theories of light-scattering were concerned with small independent particles such as gaseous systems but theories have since been evolved to account for interacting systems such as liquids and solids where the particles can no longer be considered independent. The ideas have also been extended to account for scattering from solutions of molecules which are large compared to the wavelength of light and to molecules which cannot be

considered isotropic.

The method of calculation of the scatter of a system may be approached in two ways. The first is by treating the scatter as the result of statistical fluctuations of density and concentration causing fluctuation in the optical dielectric constant. This approach is termed the Fluctuation Theory of light-scattering, was developed by Einstein[43], Schmoluchowski[44] and others and is found most useful for systems of interacting particles such as liquids and concentrated solutions. The other method is by calculation of the scatter from each independent particle followed by summation over all the particles taking into account the interference producing phase differences. This is termed the Interference Theory and was developed by Rayleigh[42] while Debye[45] showed its application to dilute non-interacting solutions of high polymers.

Rayleigh Treatment for Particles small compared to the Wavelength of Light.

When the particles comprising an ideal gas are subjected to an electric field such as that associated with a light wave having a field strength of E_0 a dipole is set up in the particle the magnitude of which is proportional to E. i.e.

$$p = \alpha E \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

where α the proportionality constant is termed the polarizability of the particle.

The equation for such an electric field may be written

$$E = E_0 \cos 2\pi(\nu t - \frac{x}{\lambda}) \quad \ldots\ldots\ldots\ldots\ldots (17)$$

where x is the position in the direction of propragation, λ is the wavelength of the light, t the time, ν the frequency and E_o the amplitude. The field is periodic and an oscillating dipole is produced.

$$p = \alpha E_o \cos 2\pi(\nu t - \frac{x}{\lambda}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (18)$$

Such an oscillating dipole is a source of radiation the amplitude of which E_s is proportional to $\frac{d^2p}{dt^2}$. If we consider a distance r from this dipole which is large compared to the wavelength of the light, the value of E_s will also be proportional to $\sin \phi_1$ where ϕ_1 is the angle between the axis of the dipole and the line from the particle to the point at distance r. Also E_s must vary inversely as r.

$$\therefore \quad E_s \propto \frac{d^2p}{dt^2} \frac{\sin\phi_1}{r}$$

It can be shown that the proportionality constant in this equation is $\frac{1}{c^2}$ where c is the velocity of light so that

$$E_s = \frac{4\pi^2\nu^2 \alpha E_o \sin\phi_1}{c^2 r} \cdot \cos 2\pi(\nu t - \frac{x}{\lambda}) \quad \ldots\ldots\ldots (19)$$

The quantity measured experimentally is the intensity which is proportional to the square of the amplitude or field strength averaged over one period of vibration. From equations (17) and (19), I_o the intensity

of the incident beam and i_s the intensity of the scattered beam are obtained. The ratio of these two quantities is

$$\frac{i_s}{I_o} = \frac{16\pi^4\alpha^2\sin^2\phi_1}{\lambda^4 r^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(20)$$

where λ, the wavelength of light in vacuo replaces $\frac{c}{\nu}$

For experimental purposes the quantity α^2 must be evaluated. It can be shown that

$$\epsilon - 1 = 4\pi N\alpha \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(21)$$

where ϵ is the dielectric constant and N the number of molecules per cubic centimetre. Also from Maxwell's electromagnetic equations

$$\epsilon = n^2$$

where n is the refractive index of the material.

$$\therefore \quad n^2 - 1 = 4\pi N\alpha \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(22)$$

Since n is close to unity, using Taylor's Theorem we may write

$$n^2 = 1 + 2\left(\frac{dn}{dc}\right)c \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(23)$$

From equations (22) and (23) we obtain

$$\alpha = \frac{\frac{dn}{dc}M}{2\pi N_A} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(24)$$

where N_A is Avogadro's Number and M the molecular weight of the particle. Using equation (24) to eliminate α from equation (20) we obtain

$$\frac{i_s}{I_o} = \frac{4\pi^2 M^2 \left(\frac{dn}{dc}\right)^2 \sin^2\phi_1}{N_A^2 \lambda^4 r^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(25)$$

For a system containing N particles per c.c.

$$\frac{i_s}{I_o} = \frac{4\pi^2 \left(\frac{dn}{dc}\right)^2 M^2 N \sin^2\phi_1}{\lambda^4 r^2 N_A^2}$$

$$\therefore \quad \frac{i_s}{I_o} = \frac{4\pi^2 \sin^2\phi_1 \left(\frac{dn}{dc}\right)^2 Mc}{\lambda^4 r^2 N_A} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(26)$$

The angular dependence of the scattered light may be seen more clearly from figure (1). The incident wave is shown plane polarised in the ZX plane. At O the oscillating dipole set up radiates a secondary wave the intensity of which varies as the square of the sine of the angle between the observer and the Z axis. This is shown diagramatically in figure (1), the lengths of the arrows being proportional to the intensity in any given direction. It is seen that this intensity is a maximum in the YX plane and falls to zero along the Z axis. Further, the scatter is symetrical about the Z axis. If we consider the incident wave to be unpolarised i.e. the

superposition of two waves plane polarised at right angles in the ZX and YX planes the distribution of scattered light is illustrated in figure (2). The vertical ZX wave behaves as described above. That polarised in the plane XY sets up a secondary wave the intensity of which is a maximum in the ZX plane, zero along the Y axis and is symetrical about the Y axis. Thus the intensity along the X axis is double that along either the Z or Y axes. For measurements in the XY plane, the intensity is a maximum at $\theta = 0^\circ$ and 180° and falls symetrically from these angles to half this value at $\theta = 90^\circ$ where θ is the angle between the incident and scattered beams. Equation (26) for unpolarised light becomes

$$\frac{i_s}{I_o} = \frac{2\pi^2\left(\frac{dn}{dc}\right)^2 Mc}{\lambda^4 r^2 N_A}(\sin^2\phi_1 + \sin^2\phi_2) \qquad \ldots\ldots(27)$$

where ϕ_2 is the angle made by the direction of observation and the dipole produced by the horizontally polarised wave.

The expression $(\sin^2\phi_1 + \sin^2\phi_2)$ may be replaced by $(1 + \cos^2\theta)$.

$$\frac{i_s}{I_o} = \frac{2\pi^2\left(\frac{dn}{dc}\right)^2 Mc(1+\cos^2\theta)}{N_A \lambda^4 r^2} \qquad \ldots\ldots\ldots\ldots\ldots(28)$$

The application of this equation to dilute solutions involves a redetermination of α^2.

For equation (22) we write

$$n^2 - n_o^2 = 4\pi N\alpha \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(29)$$

where n is the refractive index of the solution and n_o that of the solvent from which

$$n^2 - n_o^2 = 2n_o\left(\frac{dn}{dc}\right)c$$

and

$$\frac{i_s}{I_o} = \frac{2\pi^2 n_o^2 \left(\frac{dn}{dc}\right)^2 Mc(1+\cos^2\theta)}{N_A \lambda^4 r^2} \quad \ldots\ldots\ldots\ldots(30)$$

Fluctuation Theory of Scattering.

The solution may be divided into elements of volume δV whose linear dimensions are small compared to the wave-length of light of which there are N in one c.c. of solution.

$$N\delta V = 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(31)$$

The variable of composition is chosen to be c^0 the concentration of solute averaged over all the solution. The fluctuating concentration c in a volume element may be written as

$$c = c^0 + \delta c$$

where δc may be positive or negative. Due to this fluctuation in concentration there will be fluctuations in the polarizability α.

$$\alpha = \alpha^{0} + \delta\alpha$$

Substituting in equation (20) for α we obtain the equation for scatter from such a volume element.

$$\frac{i_s}{I_o} = \frac{16\pi^4(\alpha^{0}+\delta\alpha)^2\sin^2\phi_1}{\lambda^4 r^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(32)$$

Expanding $(\alpha+\delta\alpha)^2$, the only term which is unique to the solution is $\delta\alpha^2$ and since $N = \frac{1}{\delta V}$

$$\therefore \quad \frac{i_s}{I_o} = \frac{16\pi^4(\overline{\delta\alpha})^2\sin^2\phi_1}{\lambda^4 r^2 \delta V} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(33)$$

$\overline{(\delta\alpha)^2}$ is the average value of $(\delta\alpha)^2$ for a large number of elements at any instant.

$$\delta\alpha = \left(\frac{\partial\alpha}{\partial p}\right)_{T,c}\delta p + \left(\frac{\partial\alpha}{\partial T}\right)_{p,c}\delta T + \left(\frac{\partial\alpha}{\partial c}\right)_{T,p}\delta c \qquad \ldots\ldots(34)$$

Again for solution as opposed to solvent only

$$\delta\alpha = \left(\frac{\partial\alpha}{\partial c}\right)_{T,p}\delta c$$

is unique to the solution since the scatter from the solvent is subtracted from that of the solution.
Using equation (22),

$$\left(\frac{\partial\alpha}{\partial c}\right)_{T,p} = \frac{\delta V}{2\pi} n\left(\frac{dn}{dc}\right)_{T,p} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(35)$$

From equations (33) and (35),

$$\frac{i_s}{I_o} = \frac{4\pi^2 \delta V n^2 \left(\frac{dn}{dc}\right)^2 \sin^2 \phi_1}{\lambda^4 r^2} \overline{(\delta c)^2} \quad \ldots\ldots\ldots (36)$$

where $\overline{(\delta c)^2}$ is the average value of $(\delta c)^2$. This quantity depends on the way the Gibbs Free Energy of the solution varies with concentration. It can be shown that

$$\overline{(\delta c)^2} = \frac{kT}{\left(\frac{\partial^2 G}{\partial c^2}\right)_{T,p}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (37)$$

where k is Boltzmann's Constant and G is the Gibbs Free Energy.

If n_1 and n_2 are the number of moles of solvent and solute respectively in a volume δV, and $\overline{V_1}$ and $\overline{V_2}$ are the partial molal volumes then

$$n_1 \overline{V_1} + n_2 \overline{V_2} = \delta V$$

By definition $dG = \mu_1 dn_1 + \mu_2 dn_2$ where μ_1 and μ_2 are the chemical potentials of solvent and solute respectively.

$$\left(\frac{\partial G}{\partial c}\right)_{T,p} = \left(\mu_2 - \frac{\overline{V_2}}{\overline{V_1}} \mu_1\right) \frac{\delta V}{M}$$

$$\therefore \left(\frac{\partial^2 G}{\partial c^2}\right)_{T,p} = \frac{\delta V}{M}\left[\left(\frac{\partial \mu_2}{\partial c}\right)_{T,p} - \frac{\overline{V_2}}{\overline{V_1}}\left(\frac{\partial \mu_1}{\partial c}\right)_{T,p}\right]$$

By the Gibbs-Duhem equation

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

$$\therefore \left(\frac{\partial^2 G}{\partial c^2}\right)_{T,p} = -\frac{\delta V}{M}\left(\frac{n_1\overline{V_1}+n_2\overline{V_2}}{n_2\overline{V_1}}\right)\left(\frac{\partial \mu_1}{\partial c}\right)_{T,p} \qquad \ldots\ldots(38)$$

and since $\dfrac{n_2 M}{n_1\overline{V_1} + n_2\overline{V_2}} = c$

then $$\left(\frac{\partial^2 G}{\partial c^2}\right)_{T,p} = -\frac{\delta V}{c\overline{V_1}}\left(\frac{\partial \mu_1}{\partial c}\right)_{T,p} \qquad \ldots\ldots\ldots\ldots\ldots(39)$$

Substituting in equations (37) and (36)

$$\frac{I_s}{I_o} = \frac{2\pi^2 n^2\left(\frac{dn}{dc}\right)^2(1+\cos^2\theta)c}{\lambda^4 r^2\left[-\frac{1}{V_1 kT}\left(\frac{\partial \mu_1}{\partial c}\right)_{T,p}\right]} \qquad \ldots\ldots\ldots\ldots(40)$$

The equation relating chemical potential to concentration may be written as

$$\mu_1 - G_1^\circ = -RTV_1^\circ c \left(\frac{1}{M} + Bc + Cc^2 + \ldots\ldots\right) \quad ..(41)$$

where c is the concentration of the solute of molecular weight M .

Differentiating with respect to c :-

$$\left(\frac{\partial \mu_1}{\partial c}\right)_{T,p} = -RTV_1^\circ\left(\frac{1}{M} + 2Bc + 3Cc^2 + \ldots\ldots\right)$$

If $V_1^\circ = \overline{V_1}$ in dilute solution

$$\frac{i_s}{I_o} = \frac{2\pi n_o^2\left(\frac{dn}{dc}\right)^2(1+\cos^2\theta)c}{N_A\lambda^4 r^2\left(\frac{1}{M} + 2Bc + 3Cc^2 + \ldots\right)} \quad \ldots\ldots\ldots(42)$$

since $n_o^2 \approx n^2$ for very dilute solutions.

The usual method of representing this equation is to define the quantity

$$R_\theta = \frac{i_s r^2}{I_o(1+\cos^2\theta)}$$

as the Rayleigh Ratio and write

$$\frac{Kc}{R_\theta} = \frac{1}{M} + 2Bc + 3Cc^2 + \ldots\ldots \quad \ldots\ldots(43)$$

For a heterogeneous polymer sample the molecular weight average must be defined.

From equation (30), $R_\theta = K\sum_i c_i M_i$ at the limit of zero concentration where i refers to any polymer species.

$$\therefore \quad \frac{Kc}{R_\theta} = \frac{\sum_i c_i}{\sum_i c_i M_i}$$

which is the definition of the weight average molecular weight.

Light Scattering from Large Particles.

When the particle which is scattering light has a dimension comparable with the wavelength of light used interference occurs between the light waves scattered from the different parts of the molecule. The result of this is to reduce the intensity of light scattered at any angle θ other than $\theta = 0$.

A function $P(\theta)$ is defined by $P(\theta) = \frac{i_\theta}{i_0}$ where i_0 is the intensity which is scattered from a large particle at the limit of $\theta = 0$. It can be shown that, by dividing the particle up into n+1 scattering points

$$P(\theta) = \frac{1}{n^2} \sum_{i=0}^{n} \sum_{j=1}^{n} \frac{\sin \mu r_{ij}}{\mu r_{ij}}$$

where r_{ij} is the vector from the ith to the jth point and $\mu = \frac{4}{\lambda} \sin\frac{\theta}{2}$.

The behaviour of $P(\theta)$ as a function of angle depends

upon the shape of the particle i.e. rod, sphere, coil etc., but at very small values of θ it can be shown that from the variation of $P(\theta)$ with angle the radius of gyration of the particle may be obtained whatever its shape.

By expansion of $\sin\mu r_{ij}$ as a power series :-

$$P(\theta) = \frac{1}{n^2} \sum_{i=1}^{n} \sum_{j=1}^{n} \left(1 - \frac{\mu^2 r_{ij}^2}{3!} + \frac{\mu^4 r_{ij}^4}{5!} + \ldots\ldots\right)$$

Neglecting all but the first two terms of this expansion and noting that

$$\sum_{i=1}^{n} \sum_{j=1}^{n} 1 = n^2$$

in the limit of small angle

$$P(\theta) = 1 - \left(\frac{\mu^2 n^2}{3!}\right) \sum_{i=1}^{n} \sum_{j=1}^{n} r_{ij}^2$$

From calculations on the configuration of polymer chains it can be shown that

$$\sum_{i=1}^{n} \sum_{j=1}^{n} r_{ij}^2 = 2n^2\overline{\rho^2}$$

where $\overline{\rho^2}$ is the mean square radius of gyration independent of particle shape.

$P(\theta)$ may be written as

$$\underset{\theta \to 0}{P(\theta)} = 1 - \frac{\mu^2\overline{\rho^2}}{3}$$

The usual method of notation of this function is as $P^{-1}(\theta)$ so that

$$P^{-1}(\theta) = 1 + \frac{\mu^2\overline{\rho^2}}{3} \quad \text{when } \frac{\mu^2\overline{\rho^2}}{3} \text{ is small.}$$

The complete expression for $P(\theta)$ differs for particles of different shapes. The expression for random coils is

$$P(\theta) = \frac{2}{x^2}\left(e^{-x} - (1-x)\right)$$

where $x=\mu^2\overline{\rho^2}$ and applies to a monodisperse polymer sample. The correction for internal interference in the form of $P(\theta)$ may be incorporated into the equation (42).

$$\frac{Kc}{R_\theta} = \frac{1}{MP(\theta)} + 2Bc + 3Cc^2 + \ldots\ldots \qquad ..(44)$$

This equation, most commonly used in the interpretation of light scattering data, is often referred to as the Debye Equation.

It must be noted that the radius of gyration measured in this way for heterogeneous samples is a "z" average dimension.

EXPERIMENTAL.

Preparation of Polymer.

The monomer used was obtained from two sources :- Polymer Consultants Ltd. and H.Nichols Ltd.

The polymerisation was carried out for convenience in batches of around 30 mls. using an initiator. The apparatus used for polymerisation is shown in figure (3). Approximately 50 mls. of the crude monomer were placed in flask (A) and distilled under a vacuum of about 10^{-4} mm. of mercury at 40-60°C. The first and last 10 mls. were rejected and the middle fraction was collected in tube (B) into which the initiator had been weighed. Early experiments employing benzoyl peroxide as initiator produced polymers which were coloured ranging from light yellow to deep red. This was thought to be due to decomposition associated with the benzoyl peroxide. For all of the subsequent polymerisations azo-bis-isobutyronitrile was employed which produced colourless polymer.

After distillation of the monomer the reaction mixture was degassed by alternate freezing and melting. The tube was then sealed and immersed in a water bath at 60°C for varying periods of time, usually 24 to 48 hours. The weight of initiator used varied between 0.01 and 0.1 gm. Some samples were prepared by polymerising the monomer in benzene solution and in these experiments lower molecular weight material was obtained.

The polymer was freed from monomer by breaking open the reaction tube and dissolving the contents in benzene. This solution was poured into an excess of n-hexane which precipitated the polymer. After standing for some time, the liquid was decanted and the polymer dried under vacuum. The solution and precipitation processes were repeated and the polymer was freeze-dried from benzene solution.

Fractionation.

The bulk polymer as prepared contained a wide distribution of molecular weights and the purpose of fractionation procedures was to reduce such molecular heterogeneity as much as possible.

Many methods of fractionation are employed[46] and most depend on either a change in temperature or a change in solvent composition to precipitate part of the polymer from a dilute solution. The process depends upon the formation of a concentrated polymer phase in contact with the dilute solution, equilibrium being set up between the chemical potentials of the polymer in the dilute and concentrated phases. The concentrated phase preferentially contains more of the higher molecular weight material. This is indicated quantitatively by the relation

$$\frac{v_n^0}{v_n} = e^{bn}$$

where v_n^0 and v_n are volume fractions of polymer in the concentrated and dilute phase respectively. b is a function of the interaction constant between solute and solvent and n is the degree of polymerisation. e^{bn} is always positive so that at equilibrium all polymer species are more soluble

in the concentrated phase. $\frac{v_n^0}{v_n}$ increases exponentially with n and the effect of increased solubility of the polymer in the precipitated phase is enhanced for larger molecular weights. If the ratio of the volume of dilute to concentrated phase is very large then most of the low molecular weight material will be retained in the large volume of solution.

Perhaps the most common method of fractionation is to add precipitant to a dilute solution until some precipitation occurs. The precipitated layer is allowed to settle and the dilute phase is decanted. The process is repeated by adding more precipitant to the decanted liquid. This procedure unless operated on a very large scale can only produce small fractions but has the advantage that distribution curves of the original polymerisation may be constructed.[47]

In this investigation a somewhat different scheme was adopted which was similar to that used by Boyes and Strauss[48] for the fractionation of poly-4-vinyl pyridine. This involved separation of each batch of the purified polymer into three fractions by the following procedure.

The limiting viscosity number in absolute ethanol of the bulk polymer was measured. The polymer was then dissolved in about two litres of benzene to give a 1% solution. The flask was placed in a water bath at 25°C and the solution stirred vigorously. Precipitant, n-hexane, was added slowly till the solution just became turbid. After heating with the flask stoppered to redissolve the polymer, the flask was placed in a water bath and allowed to cool slowly to 25°C. The clear solution was decanted and the procedure repeated twice to obtain three fractions in all from one

polymerisation. The hexane remaining in the concentrated phase was removed under vacuum and the polymer was obtained free from solvent by freeze-drying from benzene solution.

Each batch of polymer prepared was subjected to this treatment. The limiting viscosity number for each fraction was determined in absolute ethanol and those groups of fractions with limiting viscosity numbers within 0.2 were dissolved together in benzene and a further refractionation carried out. Ten of the fractions thus obtained were kept and used for measurements. These, it was felt, would yield a fairly wide range of molecular weight over which to study the various solution properties. Table (1) shows the data obtained in the fractionation process.

Theta Solvent Measurements.

The theta solvent for a given polymer has been defined as that solvent in which the quantities $\frac{Kc}{R_\theta}$ for scattered light and $\frac{\pi}{c}$ for osmotic pressure do not change with concentration over a range of polymer concentration. In other words the solvent in which the second virial coefficient vanishes. Such a solvent may be obtained by making the temperature a Flory "θ" temperature according to the relationship[49]

$$(\mu_1 - \mu_1^\circ)_E = -RT\psi_1(1 - \frac{\theta}{T})v_2^2$$

$(\mu_1 - \mu_1^\circ)_E$ is a measure of the difference in the chemical potential existing between the polymer and solvent and it can be seen from the equation that when T, the temperature, is equal to θ this is zero. The molecules of solute in this special case assume a truly random configuration.

Another way of regarding the "Θ" temperature is as the temperature of critical miscibility at infinite molecular weight. Since the temperature of critical miscibility depends on the concentration of the polymer the "Θ" temperature depends on two variables, the molecular weight of the solute and its concentration. For a three component system comprising solvent, precipitant and polymer at a fixed temperature the quantity which is analagous to the temperature of critical miscibility in the above discussion is the solvent precipitant ratio at which precipitation just occurs. This quantity varies in like manner with concentration and molecular weight. Such a system was utilised by Schultz[30] to determine the critical consolute mixture for polystyrene in a mixed solvent comprising methyl ethyl ketone and methanol. In this investigation no single solvent could be found in which the solubility of the polymer was dependent on temperature and to obtain a "Θ" solvent it was necessary to employ a mixed solvent. Care must be taken when employing mixed solvents in light scattering measurements since preferential adsorption of one of the components by the coil can render the interpretation of results difficult. It is advantageous in such a system to employ liquids which have refractive indices close to each other.

The solvent-precipitant system chosen was n-propanol as solvent and n-heptane as precipitant of refractive indices 1.385 and 1.387 respectively. The apparatus consisted of two 5 ml. microburettes modified with "Exello" greaseless stopcocks and B10 cones to fit a 50 ml. microflask. Provision was made for stirring and the apparatus was immersed in a thermostatted tank as shown in figure (4).

Approximately 0.3 g. of one fraction of the polymer were weighed into the flask and the apparatus assembled. A minimum volume of solvent was added to dissolve the polymer and the solution process was usually complete in thirty minutes with vigorous stirring. The polymer was just precipitated by n-heptane and the volumes of solvent and precipitant used were noted. The polymer was redissolved and precipitated and the procedure repeated till the solution was very dilute. The estimation of when precipitation occurred was rendered difficult in the concentrated solutions by the high viscosity of the mixture. Local precipitation occurred due to incomplete mixing but this did not apply to the dilute solutions at lower concentrations of polymer. The whole procedure was repeated for two other fractions and with the data obtained the extrapolations required to determine the composition of the "θ" solvent were carried out as described below.

From the volumes of solvent and precipitant used, together with the weight of polymer, the weight fractions of n-propanol and polymer were calculated for each precipitation point. The curves obtained by plotting weight fraction of n-propanol against fraction of polymer are shown in figure (5). From the smoothed curves drawn for each molecular weight, the fractions of solvent at fixed concentrations of polymer were found for the three molecular weights used. These were extrapolated to infinite molecular weight by plotting the weight fraction of solvent against $\frac{1}{M^{\frac{1}{2}}}$. The lines obtained for five polymer concentrations are shown in figure (6). These were linear

facilitating the extrapolation. Using the extrapolated values of weight fraction of solvent, the line on the ternary diagram corresponding to infinite molecular weight was drawn as shown by the dotted line in figure (5). The extrapolation of this line to zero concentration furnished the composition of the "θ" solvent. In the theory of this method volume fractions are considered. Weight fractions were used here since no data was available on the density of this particular polymer. Employing the density of polystyrene however, and calculating volume fractions an identical composition was obtained. Details of the measurements and extrapolated values are shown in tables (2) and (3).

An alternative method of extrapolating the data according to Elias[50] was attempted. This involved plotting the logarithm of the fraction of precipitant against the same function of the polymer and extrapolating to the value at which the logarithm of the fraction of polymer was zero. These curves should be linear and those of different molecular weights should coincide at the extrapolated value. In effect the lines were found to be distinct curves and no extrapolation was possible.

Viscosity Measurements.

Viscosity measurements were carried out on ten fractions in absolute ethanol and in the mixed solvent. A Fitzimmons No.1 capillary dilution viscometer was used. This was immersed in a thermostatted tank controlled at 25°C to 0.01 C° and was aligned vertically by means of marks on two sides of the glass tank. Solutions were made up in 25ml. standard flasks and filtered before being added by pipette

to the viscometer. Dilutions were made by pipetting additional solvent into the viscometer and mixing after dilution was effected by bubbling dry air through the viscometer. Several times of flow between fixed marks were noted for each concentration and the average value recorded. Due to the short flow time, 34 seconds for ethanol, it was felt that kinetic energy corrections should be applied. Direct proportionality between the time of flow t and the viscosity η is only obtained if the kinetic energy correction is negligible. The general equation relating the viscosity of a solution η, to its time of flow t in a capillary viscometer may be written

$$\eta = Cdt - \frac{Bd}{t} \qquad \ldots\ldots\ldots\

The values of η were found from the measured values of t and these results are independent of kinetic energy losses.

When viscosity measurements are being made on large easily deformable molecules the viscosity should be measured at different rates of shear and extrapolated to zero rate of shear. A Couette type of viscometer is most usually employed for this type of measurement and since no such instrument was available the effect was neglected in this investigation.

The quantity of interest in a study of polymer solutions by viscometry is the limiting viscosity number. This may be defined by the quantity A in equation (46)

$$\frac{\eta - \eta_o}{\eta_o c} = A + Bc + Dc^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (46)$$

where η_o is the viscosity of the solvent and B and D are virial terms to account for interactions at higher concentrations.

Huggins has proposed the relationship :-

$$\frac{\eta - \eta_o}{\eta_o c} = [\eta] + k_1 [\eta]^2 c \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (47)$$

where k_1 is a constant which should be independent of molecular weight for a given polymer solvent system.

An alternative expression for the concentration dependence is :-

$$\frac{\ln \frac{\eta}{\eta_o}}{c} = [\eta] - k_2 [\eta]^2 c \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (48)$$

It can be shown by expansion of $\frac{\ln \frac{\eta}{\eta_o}}{c}$ as a power series that, in the limit of zero concentration :-

$$\left[\frac{\ln \frac{\eta}{\eta_o}}{c}\right]_{c\to 0} = \left[\frac{\eta - \eta_o}{\eta_o c}\right]_{c\to 0}$$

The limiting viscosity number $[\eta]$ may thus be determined by extrapolating the data according to equations (47) and (48) to zero concentration, the coincidence of the intercepts being a check on the results. The plots obtained in this way are shown in figures (8) and (9). Experimentally it has been found that the relation between the slopes of such pairs of lines leads to :-

$$k_1 + k_2 = 0.5$$

Data from the slopes of these lines are shown in table (5).

Light-Scattering Measurements.

The procedure required for light-scattering may be divided into three sections :-

1. Measurement of the refractive index increment.
2. Clarification of solutions.
3. Measurement of the intensity of scattered light.

1. Refractive Index Measurements.

Precise measurement of this quantity is of greatest importance for accurate interpretation of light-scattering data. Early attempts to determine $\frac{dn}{dc}$ by direct measurement of the refractive indices of the solvent and solution using a Pulfrich Refractometer produced results varying by 10%

from the average. This could produce errors of 20% in the determination of a molecular weight. The final and most precise values were measured on a Brice-Phoenix Differential Refractometer.

Solvent was placed in one compartment of a divided cell and solution in the other. The quantity measured was the difference in refraction of the incident beam between the solvent and solution. This was measured directly and converted to refractive index increment by previous calibration of the instrument using sucrose solutions.

Three independent solutions ranging in concentration from 0.5% to 1.5% were made up by weight and volume in 10ml. standard flasks and n, the refractive index increment was determined for each using the green line of mercury. Values of $\frac{\Delta n}{\Delta c}$ were calculated and the mean of the three values was used. In this way values of $\frac{dn}{dc}$ for poly-2-vinyl pyridine in several solvents were obtained.

These were plotted as $\frac{dn}{dc}$ against n the refractive index of solvent. The straight line obtained is shown in figure (10). By the Gladstone and Dale empirical equation :-

$$\frac{dn}{dc} = \frac{n_2}{d_2} - \frac{n_1}{d_2}$$

so that the gradient of the line in figure (10) corresponds to the reciprocal of the density of the polymer. This is calculated as 1.12 gm/c.c.

2. Clarification of Solutions.

This process is of the utmost importance in light-

scattering experiments since the presence of dust particles which are much larger than the polymer molecules cause an increase in the overall intensity of the scatter and also have a marked effect on the angular distribution of the scattered light. The effect of dust is most noticible in solvents of low refractive index e.g. water and ethanol since there is a large value of $\frac{dn}{dc}$ for the dust particles. Also, these more polar solvents are more difficult to free from dust than benzene and methyl ethyl ketone. To obtain comparatively dust free water many elaborate precautions have been taken. Normal clarification procedures may be divided into two types - filtration and centrifugation.

a) Filtration.

"Millipore" filters have been successfully used in the clarification of solutions for light-scattering. These consist of a cellulose ester membrane and their use is limited since they are dissolved by many organic solvents such as alcohols and esters.

Filtration is very slow especially when working with materials of high molecular weight.

Glass sinters are used for this purpose. They are made in five different degrees of porosity. In this work it was found that only the finest, No.5, gave reliable results. This is made to British Standard Specification with a maximum pore size of two microns. The sinters were bought as mercury filters and were modified so that pressure could be applied to the surface of the liquid in the sinter. When using the sinter it was first washed twice with the solution to avoid concentration changes caused by either previous solutions or adsorption on the glass of solute.

The solution was collected directly in the scattering cell after filtration.

b) Centrifugation.

This is the most common technique for optical clarification of solutions. Normally solutions are centrifuged for times ranging from one to two hours at speeds in excess of 10,000 r.p.m.

In the present study two makes of centrifuge were used, the Pirouette and the M.S.E. Both of these were of the angle head types. Speeds of 14,000 to 16,000 r.p.m. were employed which correspond to accelerations of 23,000 to 30,000 times that of gravity.

Usually light-scattering measurements were made on five concentrations of polymer. For this purpose a solution was made up in a standard flask and diluted by pipetting appropriate volumes of solution and solvent into stainless steel centrifuge tubes. The sixth tube was filled with solvent and pairs of tubes were balanced to within 0.1 gm. before being placed in the centrifuge. 30mls. of each solution were centrifuged and 20 mls. of the clarified solution were transferred to each scattering cell by means of a clean pipette. The main disadvantage of centrifugation as a means of clarifying solutions is that cleaning of viscous solutions is rather unsatisfactory.

Cleaning of Glassware.

All glassware after use was rinsed with the appropriate solvent to remove polymer. The glassware was then immersed in chromic acid for at least twelve hours before being washed with tap water, distilled water and stored in an oven.

The stainless steel cells after use with polymer solutions were rinsed with solvent and scrubbed with an abrasive cleaner before final rinsing and drying.

Measurement of the Intensity of Scattered Light.

The instrument used was marketed by S.O.F.I.C.A. and is based on an original design developed by Wippler and Scheibling[51]. The principal arrangements are shown diagramatically in figure (11). The light source is a Philip's S.P. water cooled, high pressure mercury lamp and the green line of wavelength 5460 A°, isolated by filters, was employed throughout the investigation. The main distinctive feature of this instrument is that the scattering cell is suspended in a bath of benzene thus eliminating large refraction effects at the outside surface of the cell.

Measurements of the light scattered from one concentration of solution were made at eleven predetermined angles. Depolarisation measurements were effected on this instrument by means of glazebrook prisms incorporated in the incident beam. As expected depolarisation from such large molecules was negligible and the molecules were considered to be isotropic.

Reference Standard.

Initial standardisation of the instrument was carried out by the manufacturers using a dust free sample of purified benzene contained in a sealed glass cell. The scatter of a cylindrical glass block was measured against this standard benzene and this glass block was used as a sub-standard in most subsequent investigations. The disadvantage of using a solid for a scattering standard was that no check could be

made on the performances of the instrument at angles other than 90^{o}. To overcome this, some benzene was dried and distilled several times in a closed system and, after copious rinsing of a cell with the distillate, a sample was sealed in the cell and used for instrument checks.

Treatment of Results.

Three main quantities may usually be determined from light-scattering data. These are the molecular weight, the principal dimension and the second virial coefficient. An outline of the theory underlying the measurement of these quantities has been given above. In all cases the results obtained were treated by the method proposed by Zimm[12]. This enables all the measured data to be represented graphically and these quantities determined directly.

The intensity of scatter for the solvent I was subtracted from the intensity at the same angle for the solution I to give the scatter due to the polymer $I-I_o$. To account for the depolarisation of scattered light and change in the volume of solution scattering with angle, $I-I_o$ was multiplied by a factor $\propto = \frac{\sin\theta}{1+\cos^2\theta}$. Finally the quantity $\frac{c}{(I-I_o)\propto} = \frac{c}{I_S}$ was calculated for each angle and concentration.

The Debye Equation was used to represent the data.

$$\frac{Kc}{R_\theta} = \frac{1}{MP(\theta)} + 2Bc \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (49)$$

The data were plotted as $\frac{c}{I_S}$ against $k^{0}c + \sin^2\frac{\theta}{2}$ where k^{0} is

an arbitrary constant used merely to obtain clear representation of the data. Extrapolation of the data to zero concentration and zero angle is readily performed using this type of plot and it is the extrapolated values which are used in the calculation of molecular weights and dimensions. Figures (12) and (13) are examples of the type of plots obtained.

1. Molecular Weight.

$P^{-1}(\theta)$ in equation (49) is a function of $\sin^2 \frac{\theta}{2}$.

In the limit of $\theta = 0$, $P^{-1}(\theta) = 1$.

$\therefore$ At zero angle and zero concentration $\frac{Kc}{R_\theta} = \frac{1}{M}$.

Since the Rayleigh Ratio of two species is proportional to the intensity of light which they scatter and since the arbitrary standard used, benzene, scattered 100 :-

$$R_{\theta solute} = \frac{R_B I_S}{100}$$

The molecular weight is determined experimentally from the equation :-

$$\frac{1}{M} = 50.6 \left(\frac{dn}{dc}\right)^2 \left[\frac{c}{I_S}\right]_{c=0,\theta=0}$$

where 50.6 incorporates the dimensions of the machine and the optical constants.

For a given polymer-solvent system :-

$$M = \frac{K''}{\left[\frac{c}{I_S}\right]_{c=0,\theta=0}}$$

2. **Radius of Gyration.**

When c=0 equation (49) may be written :-

$$\frac{Kc}{R_\theta} = \frac{1}{MP(\theta)}$$

$$\therefore \quad \frac{K^{0}c}{I_S} = \frac{1}{M} P^{-1}(\theta)$$

As was shown above

$$P^{-1}(\theta) = 1 + \frac{\mu^2\overline{\rho^2}}{3}$$

at low values of θ, where $\mu = \frac{4}{\lambda}\sin\frac{\theta}{2}$. The slope of the $c = 0$ line at low angles is given therefore by :-

$$K^{0} \frac{d\left[\frac{c}{I_S}\right]}{d(\sin^2\frac{\theta}{2})} = \frac{1}{M}\frac{\overline{\rho^2}}{3}\frac{16\pi^2}{\lambda^2}$$

In the limit of zero angle $K^{0} = \frac{1}{M\left[\frac{c}{I_S}\right]}$

If the gradient of the zero concentration line at low angles is termed G_1

$$\therefore \quad \frac{G_1}{\left[\frac{c}{I_S}\right]_{\theta=0,\,c=0}} = \frac{\overline{\rho^2}16\pi^2}{3\lambda^2}$$

Assuming a perfectly gaussian distribution of segments where $\langle R^2 \rangle = 6\overline{\rho^2}$

then

$$\frac{G_1}{\left[\frac{c}{I_S}\right]_{\theta=0,\,c=0}} = \frac{8}{9}\frac{\pi^2}{\lambda^2}\left\langle R^2\right\rangle$$

3. <u>Second Virial Coefficient, B.</u>

When $\theta=0$ equation (49) may be written :-

$$\frac{Kc}{R_\theta} = 2Bc + \frac{1}{M}$$

If the gradient of the zero angle line is termed G_2.

$$K'G_2 = 2B$$

$$\therefore \quad B = \frac{G_2K'}{2}$$

The quantities M_w, $\left\langle R^2\right\rangle_z$ and B were determined for each fraction of the polymer in two solvents. The results are listed in table (6).

DISCUSSION.

The discussion of this investigation will be divided into three sections where the results may be interpreted in the light of theory and previous investigations of a similar type. The three sections may be considered as 1) Relationships between limiting viscosity number and molecular weight. 2) Dependence on molecular weight of the molecular dimensions and of the second virial coefficients. 3) Agreement of experiment with relationships involving viscosity, molecular dimensions and molecular weight.

Polydispersity.

One fundamental difficulty in an investigation of this type is the absence of precise knowledge concencerning the polydispersity of the samples under investigation. Although fractionation is usually carried out preparatory to measurements, it is by no means certain that the fractions obtained are even approximately monodisperse. In some investigations no estimate is made of the polydispersity while in a similar investigation of poly-4-vinyl pyridine by Berkowitz, Yamin and Fuoss[52] a polydispersity of $M_z:M_w:M_n = 3:2:1$ is quoted which corresponds to the normal distribution obtained for an "autopolymerisation" before fractionation. This is explained by the proposal that the polymer degrades in solution. For the present investigation a similar polydispersity will be assumed mainly because of the difficulty of interpreting the data if the fractions are assumed monodisperse and also from estimates of $M_w:M_n$ ratios based on the method of treatment of light-scattering data produced by Benoit[25].

Since careful fractionation of the bulk polymer was carried out only the following explanations can be suggested for the wide molecular weight distribution obtained. Firstly, that the initial polymerisations were made to rather high conversion and secondly that the method of grouping the fractions is inferior to that of fractionating a large sample into comparatively small portions.

1. Viscosity Molecular Weight Relationships.

As described in the introduction Staudinger proposed the first relationship of direct proportionality between viscosity and molecular weight. The semi-empirical equation now accepted is that proposed by Mark and Houwink[8,9] which may be written as :-

$$[\eta] = KM^a$$

The exponent a depends upon the solvent and upon the shape of the molecule e.g. for a rod a=2 and for a random coil, a=0.50. For a heterogeneous sample of a polymer the molecular weight average involved is the viscosity average which lies between M_n and M_w. The usefulness of such an equation is obvious when one considers the relative ease with which viscosity measurements can be made. Care must be taken however since the equation, once the constants have been established, can strictly be applied only to those samples which have a similar molecular weight distribution to those used for the calibration. This is apparent when one observes the number of equations which have been obtained for the same polymer solvent systems by different workers. Attention is drawn to this by Onyon[53] who quotes results for polyacrylonitrile. In this investigation the molecular weights obtained for each

of the fractions in the two solvents were averaged and this average was used in a plot of $\log[\eta]$ against log M. These plots are shown in figure (14). The lines are seen to be straight over a range of molecular weight of 9×10^4 to 5×10^6. Although K and a are usually found to be independent of molecular weight, some investigators[54,55] have found that such data can best be represented by two straight lines each covering a different molecular weight range.

The equations obtained for the viscosity molecular weight relationships in the two solvents are :-

Ethanol $$[\eta] = 2.8 \times 10^{-4} M^{0.66} \quad \ldots\ldots\ldots\ldots\ldots\ldots (50)$$

Mixed Solvent
$$[\eta] = 1.2 \times 10^{-3} M^{0.50} \quad \ldots\ldots\ldots\ldots\ldots\ldots (51)$$

Although at present no work has been published on such a relationship for poly-2-vinyl pyridine in ethanol, that for the isomer 4-vinyl pyridine has been reported by two sets of investigators. In absolute ethanol the equation obtained by Berkowitz, Fuoss and Yamin was[52] :-

$$[\eta] = 2.5 \times 10^{-4} M^{0.68}$$

which is in very good agreement with that obtained in this work. Boyes and Strauss[48] however using ethanol containing 8% water obtained the equation :-

$$[\eta] = 1.2 \times 10^{-4} M^{0.73}$$

This equation is somewhat different from either of the previous two. The larger value of a is unexpected since water is a precipitant for poly-vinyl pyridines and any ethanol water mixtures should be poorer solvents than pure ethanol resulting in an exponent closer to 0.50 and a larger value of K. Quite the reverse is seen to be the case.

Equation (51) indicates that the mixed solvent was apparently a true "Θ" solvent since the exponent of 0.50 is that predicted theoretically for such a solvent. Strauss[48] has compared the molecular dimensions of poly-4-vinyl pyridine to those of polystyrene. If we assume that the analogy is correct it is seen that the value of K for poly-2-vinyl pyridine is about 50% higher than that obtained by most workers[56] for polystyrene in a "Θ" solvent. This could be due to two factors. The first is that poly-2-vinyl pyridine in contrast to polystyrene has some polyelectrolyte properties as indicated by Cashin[57]. This may render the analogy to polystyrene somewhat inaccurate. Alternatively if the polydispersity is 3:2:1 and the viscosity average lies between M_w and M_n this correction will affect the value of K in such a way as to reduce it, bringing it into agreement with the literature on polystyrene.

2. Molecular Dimensions.

Light scattering at present furnishes the only absolute method for determining the dimensions of molecules in solution and is limited to molecules having one dimension between $\frac{\lambda}{20}$ and λ where λ is the wavelength of light used. Two methods can be employed to determine molecular dimensions. Earlier workers used dissymmetry measurements

i.e. the ratio of scattered light at angles symmetrical about 90°. On extrapolation of the dissymmetry to zero concentration the limiting value obtained enabled the molecular size to be determined from tables compiled by Doty and Steiner[14]. The alternative and more modern method is to determine the slope of the $\left(\frac{Kc}{R_{\theta}}\right)_{c=0}$ line of the Zimm Plot which gives the radius of gyration. This latter method is adopted in this investigation. A review of the methods, with results obtained, has been given by Peaker[58].

For each fraction of polymer in the two solvents, the mean square radii of gyration were measured. Normal practice in such investigations is to quote molecular sizes as $\langle R^2 \rangle$, the mean square end to end distance. This is usually obtained by employing the relationship :-

$$\langle R^2 \rangle = 6\langle \rho^2 \rangle$$

which is strictly applicable only for coils whose configuration is gaussian. In practice this is true in the theta solvent. In good solvents, however, the coil is swollen by solvent polymer interactions and more extended configurations are obtained.

Peterlin[59] has given a method whereby the true values of $\langle R^2 \rangle$ may be obtained by measuring the limiting slope of the $\frac{Kc}{R_{\theta}}_{c=0}$ line and calculating the value of $\langle R^2 \rangle$ as described above. Using the molecular weight dependence of $\langle R^2 \rangle$ a value for ν in the equation :-

$$\langle R^2 \rangle = KM^{1+\nu}$$

is calculated. By expansion of the expression for $P(\theta)$ utilising an expression for non-gaussian distribution of segments the relationship :-

$$\langle R_T^2 \rangle = \langle R^2 \rangle \left(1 + \frac{5\nu}{6} + \frac{\nu^2}{6}\right)^{\frac{1}{2}}$$

is obtained where $\langle R_T^2 \rangle$ is the true mean square end to end distance of the molecule .

Alternative methods of dealing with the problem of relating $\langle R^2 \rangle$ and $\langle \rho^2 \rangle$ have been described by Benoit[25], Hyde[26] et alia who have shown methods whereby the value of $\langle R^2 \rangle$ can be obtained from the curvature of the $P^{-1}(\theta)$ curve for a single polymer fraction. The nett result of performing these corrections to the experimental $\langle \rho^2 \rangle$ obtained is slight, being comparable in magnitude with the experimental uncertainty in the measurement. For this reason the quantity quoted here as the molecular dimension is $6\langle \rho^2 \rangle$ thus keeping the sizes in accord with those obtained by other investigators while adopting the reasonable assumption that the deviation of the segment distribution from gaussian is small.

The variation of $\langle R^2 \rangle$ with molecular weight is shown in figure (15). These plots show that the sizes of the various fractions in ethanol are much larger than sizes of corresponding fractions in the mixed solvent. The distinct upward curvature of the curve for ethanol indicates that the molecular size is increasing faster than linearly with M in accordance with excluded volume theory. In the supposed ideal solvent however there still seems to be some upward curvature even if allowance is made for the experimental error.

This indicates that the composition of the mixed solvent is to some extent better than an ideal solvent. A more sensitive test of ideality of solvent is to plot the values of $\langle R^2 \rangle$ and M on logarithmic scales and to measure the gradient of the line obtained.

Zimm, Stockmayer and Fixman[23] in 1953 summarised the then current thought concerning the $\langle R^2 \rangle$- M relationship and concluded on the basis of theory and experiment that $\frac{\langle R^2 \rangle}{M}$ does not reach an upper limit as M increases without limit. This may be written as :-

$$\langle R^2 \rangle = KM^{1+\nu} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

where ν is positive. A double logarithmic plot of $\langle R^2 \rangle$ against M therefore, furnishes as gradient the value of $1+\nu$. In a theta solvent ν is zero.

The plots obtained are shown in figure (16) and the lines shown correspond to the following equations :-

In ethanol $\qquad \langle R^2 \rangle_z = 0.063\ M_w^{1.25} \qquad \ldots\ldots\ldots\ldots (52)$

In mixed solvent $\qquad \langle R^2 \rangle_z = 0.49\ M_w^{1.08} \qquad \ldots\ldots\ldots\ldots (53)$

From the latter equation it can be seen that the mixed solvent is not a true theta solvent since the estimated error in the gradient of the lines is $\pm$ 0.02 so that even allowing for maximum error the theoretical value for the gradient of 1.00 is not obtained.

Another method used for the evaluation of ν in the R^2-M equation depends on the exponent "a" in the viscosity molecular weight equation.

By the Flory and Fox Theory :-

$$[\eta] = \frac{\Phi \langle R^2 \rangle^{3/2}}{M}$$

$$\therefore \quad \langle R^2 \rangle = \left(\frac{M[\eta]}{\Phi} \right)^{2/3}$$

Since $\langle R^2 \rangle = K_1 M^{1+\nu}$ we may write

$$\frac{M^{2/3}[\eta]^{2/3}}{\Phi^{2/3}} = K_1 M^{1+\nu}$$

$$\text{or} \quad [\eta] = K_2 M^{\frac{1}{2}(1+3\nu)}$$

By analogy with the relation :-

$$[\eta] = KM^a$$

$$a = \tfrac{1}{2}(1+3\nu)$$

From the viscosity molecular weight relationship $a=0.66$.

$$\therefore \quad \nu \doteq 0.1$$

This value of the exponent is seen to be much smaller than that obtained by direct measurement of the variation of $\langle R^2 \rangle$ with M. One possible explanation for this is that the deviation of the distribution of segments in the molecule from gaussian alters the flow behaviour of the solvent through the molecule appreciably and that the reasoning

indicated above is not strictly applicable to large molecules exhibiting excluded volume. It was also considered that the use of $\langle R^2 \rangle_z$ with M_w might yield too high a value for ν. To determine the truth of this a separate estimate of the polydispersity of each fraction was made and the values of M_n and $\langle R^2 \rangle_n$ determined as indicated using the method developed by Benoit [25].

The expression for $P^{-1}(\theta)$ in a polydisperse system exhibiting excluded volume is, at large angles,

$$P^{-1}(\theta) = \frac{N_w}{N_n} \frac{\sqrt{2\varepsilon}}{2\varepsilon(\sqrt{\varepsilon})^2} + \left(\frac{\mu^2 b^2}{6}\right)^{\varepsilon} \frac{N_w}{2\varepsilon\sqrt{\varepsilon}}$$

where $\frac{1}{\varepsilon} = 1+\nu$, b is the bond length and N the degree of polymerisation. In this treatment the distribution of segments in the coil is assumed gaussian and it can be shown that :-

$$\frac{\Delta P^{-1}(\theta)}{\Delta \sin^2\frac{\theta}{2}\ (\text{Intercept})} = \frac{\sqrt{\varepsilon}}{\sqrt{2\varepsilon}} \left(\frac{\langle R^2 \rangle_n 4^2 \pi^2 b^2}{6\lambda^2}\right)^{\varepsilon}$$

This refers to the asymptote to the $P^{-1}(\theta)$ line at high values of θ and the intercept referred to is the intercept of this asymptote on the $P^{-1}(\theta)$ axis from which can be calculated the number average degree of polymerisation and thus the molecular weight.

$$\text{Intercept} = \frac{N_w}{N_n} \frac{\sqrt{2\varepsilon}}{2\varepsilon(\sqrt{\varepsilon})^2}$$

From the viscosity reasoning $\xi = 0.9$ and from tables the value of $\frac{\Gamma 2\xi}{\Gamma \xi}$ was estimated to be 0.87. From this data and a knowledge of the weight average molecular weight the values of M_n and $\langle R^2 \rangle_n$ were calculated for each fraction.

To account for excluded volume $P^{-1}(\theta)$ was plotted as a function of $\left(\sin^2\frac{\theta}{2}\right)^{0.9}$ and the slope and intercept of the asymptote to the line at large θ were used in the above equations.

The values of M_n and $\langle R^2 \rangle_n$ obtained together with the $\frac{M_w}{M_n}$ ratio are shown in table (6). A double logarithmic plot of these quantities produced a line of equation :-

$$\langle R^2 \rangle_n = 0.027\, M_n^{1.24} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (54)$$

The identical gradient obtained showed that the exponent in the relation is independent of the averages used if the fractions are of fairly constant polydispersity.

On examining the literature for similar data it was found that similar equations have been produced for R^2-M relationships by other authors. Notley and Debye[60] for polystyrene in toluene obtain :-

$$\langle R^2 \rangle = 0.038\, M^{1.22}$$

and the data of Berkowitz, Yamin and Fuoss[52] for poly-4-vinyl pyridine can be fitted quite well by equation (50) above.

It would appear therefore, from this evidence that the value of ν as estimated by R^2-M measurements has a somewhat

different significance to that obtained by viscosity considerations.

A further point of interest in the R^2-M equations is that the lines corresponding to the equation for different solvents cross at positive values of M. This value of $M = 7 \times 10^4$ is too large to assume that the molecules are behaving in any other way than as random coils. At present no satisfactory explanation can be proposed for this, apart from the suggestion that the equation applies only over a limited range in molecular weight.

Estimation of Hindrance to Rotation.

As indicated in the introduction the expression for the mean square end to end distance in an unperturbed polymer coil may be written :-

$$\langle R_o^2 \rangle = nl^2 \frac{1-\cos\theta}{1+\cos\theta} \cdot \frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}}$$

If the expression relating $\langle R^2 \rangle$ to M is employed in equation (7) the following equation is obtained :-

$$\langle R^2 \rangle = \left(\frac{M}{m}\right)^{1+\nu} l^2 \frac{1-\cos\theta}{1+\cos\theta} \cdot \frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}} \quad \ldots\ldots\ldots(55)$$

where M is the molecular weight of the polymer and m is half the monomer weight. It may be mentioned that $\cos\theta$ appears in this equation because there is only one type of valence angle to consider. In polymers containing more than one type of atom in the chain an average value of $\cos\theta$ must be used.

Substituting for $\langle R^2 \rangle$ from equation (7).

$$KM^{1+\nu} = \left(\frac{M}{m}\right)^{1+\nu} l^2 \frac{1-\cos\theta}{1+\cos\theta} \cdot \frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}} \quad \ldots\ldots(56)$$

For poly-2-vinyl pyridine,

$$m = 52.5, \quad \frac{1-\cos\theta}{1+\cos\theta} = 2.00 \quad \text{and} \quad l = 1.55A^{\circ}$$

In ethanol therefore, with K = 0.063,

$$\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}} = \frac{0.063 \times 52.5^{1.25}}{4.8} = 1.97$$

In the mixed solvent with K = 0.49,

$$\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}} = \frac{0.49 \times 52.5^{1.08}}{4.8} = 7.3$$

From the above reasoning and calculation it is seen that there is more hindrance to rotation in the poor solvent than in the good solvent. This may be due to the more expanded configuration of the chain in ethanol. This also indicates that the effect of solvent cannot be completely separated from the "skeletal" effects due to short range interactions. The effect of polydispersity is discounted here since the differences refer to solvent and not to samples of polymer used.

<u>True Unperturbed Dimensions.</u>

As discussed above the composition of the mixed solvent obtained by precipitation measurements corresponded to a solvent slightly better than ideal.

An additional criterion of such a solvent is one in which the zero angle line of the Zimm Plot has zero gradient at low values of concentration. By plotting $\langle R^2 \rangle^{\frac{1}{2}}$ against B and extrapolating linearly to B=0 a value of the unperturbed $\langle R^2 \rangle^{\frac{1}{2}}$ was obtained for each fraction. While no full theoretical justification can be made for linear extrapolation, such a relationship between $\langle R^2 \rangle^{\frac{1}{2}}$ and B has been reported by other workers[61].

The lower lines in figures (15) and (16) correspond to the extrapolated values obtained. In figure (15) the plot of R^2/M is linear and the equation obtained from the lower plot in figure (16) is :-

$$\langle R_o^2 \rangle = 1.1\ M^{1.00} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (57)$$

Krigbaum[62] has shown a method whereby the unperturbed dimensions can be calculated from a knowledge of viscosity, molecular weight and second virial coefficient in a good solvent. The method was employed here to compare the results with the empirical extrapolation described above. Use is made of the equation

$$[\eta] - [\eta_\theta] = 5 \times 10^{-3}\ BM$$

to calculate $[\eta_\theta]$ and thus to find K in the equation

$$[\eta_\theta] = KM^{0.50}$$

The unperturbed dimensions are then calculated from :-

$$\frac{\langle R_o^2 \rangle}{M} = \left(\frac{K}{\Phi}\right)^{2/3} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (58)$$

Since in this investigation the viscosity data seem to correspond to a true theta solvent the values of $[\eta]-[\eta]_\theta$ obtained experimentally were plotted against BM for the various fractions. The points could be fitted fairly well into a straight line passing through the origin of gradient approximately 5×10^{-3} so that the value of K used in equation (58) was 1.2×10^{-3}. Φ was taken as 2.1×10^{21} from various literature values.

$$\therefore \quad \frac{\langle R_o^2 \rangle}{M} = \frac{1.2 \times 10^{-3}}{2.1 \times 10^{21}}^{2/3}$$

Converting units of dimensions from centimetres to angstroms :-

$$\frac{\langle R_o^2 \rangle}{M} = 0.665$$

This refers to a monodisperse sample. If it is assumed that in this case,

$$\frac{\langle R_o^2 \rangle_z}{\langle R_o^2 \rangle_w} = 1.5 \qquad \text{then} \qquad \frac{\langle R_o^2 \rangle_w}{M_w} = 1.00$$

It is seen that this agrees with the value obtained from equation (57). Using the extrapolated values for the unperturbed molecular dimensions a value of 12 is obtained for the term $\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}}$ in equation (56).

The general trend of the magnitude of this term with solvent is illustrated below. Values of $\overline{\cos\phi}$ are also shown.

Solvent	$\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}}$	$\overline{\cos\phi}$
Ethanol	1.97	0.327
Mixed Solvent	7.3	0.758
θ Solvent	12.0	0.847

If a similar calculation is employed on results obtained for polystyrene by Notley and Debye[60] the following results are obtained.

Solvent	$\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}}$	$\overline{\cos\phi}$
Toluene	1	0
Cyclohexane 43°	14.3	0.870
Cyclohexane 34°	12.4	0.850

The general effect of solvent is corroborated since $\overline{\cos\phi}$ increases as the solvent tends to a "θ" solvent.

Second Virial Coefficients.

The relationship existing between the second virial coefficient and the extension of the polymer coil is not completely understood but, as is seen from table (6), the general prediction that there is a correlation between the size of the molecule and this quantity is verified. The results show that the values of B obtained in the mixed solvent are very much smaller than those in ethanol which is classed as a good solvent for the polymer. The fact that B has a small positive value in this solvent is a further indication that the mixed solvent was not an exact theta solvent.

The effect of B reaching a zero value in a theta solvent has been discussed as a method of determining the composition of such a solvent [63]. It is felt however that the experimental accuracy required to determine the composition by measuring the value of B in solvents of different composition would be greater than that obtainable in most cases.

Molecular Weight Dependence of B.

Although it can be shown theoretically that the values of B should depend on molecular weight some authors report B independent of M. Berkowitz, Yamin and Fuoss[52] found for poly-4-vinyl pyridine a value of 4×10^{-4} for a series of molecular weights. In the present investigation however it is found that B increases as molecular weight decreases and the data can best be represented by the equation :-

$$B = 2.5 \times 10^{-3} M^{-0.41}$$

3. Comparison of Experimental Data with Hydrodynamic Theories.

As outlined in the introduction it can be shown that :-

$$[\eta] = \Phi \frac{\langle R^2 \rangle^{3/2}}{M}$$

where Φ should be a constant independent of solvent and polymer. In order to calculate the values of Φ it is necessary to convert the quantities $\langle R^2 \rangle_z$ and M_w to the same average, the number average, and substitute in the above equation. The values obtained for the fractions in ethanol

are shown in table (6) and the average 2.2×10^{21} is seen to lie close to the accepted value of 2.1×10^{21}.

Expansion Factor α.

While the Flory parameter α accounts for the difference in molecular size between the calculated values of a polymer chain and the experimental, its nature and physical significance is still a matter for some discussion. Flory and Krigbaum in an attempt to relate α to the physical excluded volume characterised the interaction between polymer and solvent by heat and entropy parameters. The resulting equation may be written as :-

$$\alpha^5 - \alpha^3 = CM^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(57)$$

where C is a complex constant. According to this equation the quantity $\frac{\alpha^5 - \alpha^3}{M^{\frac{1}{2}}}$ should be invariant with molecular weight.

Values of this quantity are shown in table (7) where it is seen that there is distinct upward trend over the molecular weight range considered. This is in keeping with other experimental tests of this equation[64]. Other workers[65] have produced the equation :-

$$\alpha^5 - \alpha^4 = KM^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(58)$$

in place of equation (57). The results of this study calculated according to (58) are also listed in table (8).

TABLE 1. Grouping of Fractions.

Sample and 1st.Fraction No.	L.V.N.	2nd Fraction No.	L.V.N.	Ref.No.
A 1-1	5.8	B 1-1		
		1-2	5.60	2
		1-3		
A 10-1	5.3	B 2-1	6.30	1
11-1	5.3	2-2		
		2-3		
A 14-1	5.1	B 3-1		
12-1	5.0	3-2	4.06	
2-1	5.0	3-3		
3-1	5.0			
A 17-1	4.7	B 4-1		
15-1	4.7	4-2	4.17	3
		4-3		
A 16-1	3.8	B 6-1		
10-2	3.8	6-2	3.45	4
		6-3		
A 6-2	3.41	B 7-1		
1-2	3.40	7-2	3.14	5
7-1	3.40	7-3		
9-1	3.35			
8-1	3.24			
12-2	3.25			
11-2	3.42			

Sample and 1st.Fraction No.	L.V.N.	2nd Fraction No.	L.V.N.	Ref.No.
A 2-2	2.78	B 8-1		
5-1	2.92	8-2	2.51	6
15-2	2.70	8-3		
A 2-3	2.00	B 10-1		
4-1	1.90	10-2	1.66	7
6-3	1.86	10-3		
3-2	1.80			
7-2	2.00			
13-1	1.66			
10-3	1.70			
11-3	2.00			
A 8-2	1.40	B 11-1		
4-2	1.20	11-2	1.50	8
13-2	1.40	11-3		
15-3	1.30			
12-3	1.40			
A 13-3	0.82	B 12-1		
16-3	1.10	12-2	1.15	9
		12-3		
A 8-3	0.40	B 13-1	0.62	10
		13-2		
		13-3		

Θ-solvent Calculation.

TABLE 2.

Fraction No.	1	5	10
$M_w \times 10^{-6}$	4.5	1.35	0.086
$\left(\frac{1}{M}\right)^{\frac{1}{2}} \times 10^4$	4.71	8.3	34

TABLE 3.

Conc. Polymer	Wt. Fract. n-propanol			
	Fr.1	Fr.5	Fr.10	$M=\infty$
0.01	0.4065	0.4023	0.3940	0.4080
0.02	0.4103	0.4073	0.3960	0.4129
0.03	0.4138	0.4103	0.3970	0.4120
0.04	0.4166	0.4130	0.3979	0.4200
0.05	0.4190	0.4150	0.3980	0.4230
0.06	0.4210	0.4166	0.3984	0.4252

Extrapolated value of Wt. Fract. propanol at zero concentration and infinite molecular weight is 0.404

Density n-propanol 0.799
Density n-heptane 0.679

Composition of Θ-solvent by volume fractions :-

n-propanol 0.365
n-heptane 0.635

TABLE 4. Viscosity Results on Pure Liquids.

Liquid	Viscosity (c.p.)	Time (secs.)	Density gm/ml.
Methanol	0.5445	18.96	0.793
Benzene	0.6028	19.02	0.879
Water	0.8903	23.85	0.998
Ethanol	1.078	35.48	0.789
Propanol	2.004	61.22	0.799

TABLE 5. Viscosity Results on Polymer Solutions.

Fr.No.	Ethanol				θ-solvent			
	$[\eta]$	k_1	k_2	k_1+k_2	$[\eta]$	k_1	k_2	k_1+k_2
1	6.30	0.510	0.097	0.607	2.42	0.327	0.171	0.498
2	5.6	0.298	0.120	0.409	2.17	0.276	0.233	0.521
3	4.17	0.395	0.160	0.555	1.73	0.372	0.149	0.521
4	3.45	0.390	0.150	0.450	1.59	0.364	0.155	0.519
5	3.14	0.330	0.174	0.504	1.35	0.312	0.195	0.507
6	2.51	0.285	0.183	0.468	1.10	0.136	0.358	0.504
7	1.66	0.275	0.235	0.510	0.90	0.238	0.268	0.506
8	1.50	0.305	0.204	0.509	0.77	0.116	0.386	0.502
9	1.15	0.162	0.330	0.492	0.63	0.274	0.344	0.618
10	0.62	0 —	—	—	0.34	0.00	0.66	0.66

TABLE 6. Light-Scattering Results.

Ethanol

Fraction No.	M_w x10^{-6}	$\langle R^2 \rangle_z$ x10^{-6}	B x10^4	M_n x10^{-6}	$\langle R_n^2 \rangle$ x10^{-6}	Φ x10^{-21}	$\frac{M_w}{M_n}$
1	4.50	13.50	1.97	2.86	5.48	1.48	1.3
2	3.17	8.75	2.10	1.71	3.05	1.83	1.8
3	2.18	5.45	2.03	1.23	2.14	1.75	1.7
4	1.69	3.72	2.36	0.82	1.21	2.04	2.1
5	1.35	3.08	3.0	0.64	0.985	2.07	2.1
6	0.85	1.50	2.8	0.40	0.51	3.00	2.1
7	0.57	1.01	4.45	0.26	0.296	2.28	2.2
8	0.47	0.770	4.6	0.22	0.238	2.58	2.1
9	0.345	0.655	5.0	0.153	0.191	1.97	2.2
10	0.086	–	19.0	–	–	–	–

Mixed Solvent

1	4.5	7.63	0.6			1.34	
2	3.2	5.65	0.5			1.33	
3	1.9	3.17	0.7			1.64	
4	1.57	2.28	0.5			1.97	
5	1.39	1.89	0.4			1.85	
6	0.835	1.16	0.4			2.01	
7	0.518	0.673	0.5			2.32	
8	0.42	0.615	0.3			1.85	
9	–	–	–			–	
10	–	–	–			–	

TABLE 7. Values of $\frac{\alpha^5-\alpha^3}{M^{\frac{1}{2}}}$ in Two Solvents.

$M.10^{-6}$	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5
$\frac{\alpha^5-\alpha^3}{M^{\frac{1}{2}}}.10^3$									
Ethanol	3.93	4.00	4.27	3.84	3.44	3.38	3.30	2.91	3.91
$\frac{\alpha^5-\alpha^3}{M^{\frac{1}{2}}}.10^4$									
Mix.Solv.	6.28	5.85	5.35	5.50	5.56	4.94	4.40	3.60	4.50

TABLE 8. Values of $\frac{\alpha^5-\alpha^4}{M^{\frac{1}{2}}}$ in Two Solvents.

$M.10^{-6}$	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5
$\frac{\alpha^5-\alpha^4}{M^{\frac{1}{2}}}.10^3$									
Ethanol	2.46	2.50	2.64	2.36	2.10	2.04	1.90	1.71	2.40
$\frac{\alpha^5-\alpha^4}{M^{\frac{1}{2}}}.10^4$									
Mix.Solv.	3.40	3.30	3.32	3.01	3.03	2.76	2.41	1.93	1.92

CONCLUSIONS.

While the behaviour of poly-2-vinyl pyridine in solution conforms fairly well to that of a linear vinyl polymer, attention might be drawn to several points.
1. The most reliable method of determining the composition of an "ideal" solvent is the thermodynamically well founded precipitation method. In this investigation however the results of measurements on three fractions of very widely separated molecular weight produced a mixed solvent in which molecular weight dependence of molecular dimensions tended more to that in a good solvent. This might be explained on the basis that the liquids used differed considerably in polarity and that, since the polymer itself is slightly polar, selective adsorption of n-propanol took place close to the segments of polymer so that the solution in the neighbourhood of the coil was in effect richer in the good solvent. Due to the closeness of the refractive indices this would not affect the molecular weight obtained but would merely tend to expand the coil.

In contrast to the molecular weight dependence of the dimensions, that of the viscosity is typical of that expected in a true theta solvent. Only in one other case has such an occurrence been repeated and that was ascribed to the nature of the polymer[66].

One further explanation of the non-ideality of the mixed solvent could be that measurements on the molecular dimensions were made at a temperature below 25°C. Subsequent experiment showed that the polymer precipitated on heating a solution of the polymer in the mixed solvent. This could explain why the mixed solvent is a better solvent

below 25°C and also why the viscosity measurements at 25°C give the correct exponent. Since the temperature control on the light-scattering apparatus was not sensitive at room temperatures no verification of this was made.

2. The values of the hindered rotation term seems to decrease with "goodness" of solvent for a given polymer. This has not been reported before due perhaps to the tendency in such investigations against making allowance for excluded volume effects. It is reasonable however to assume that, as the chain takes up a more expanded configuration, there will be more freedom for large side groups to rotate.

3. Although the average value of $\bar{\Phi}$ in table (6) is close to that obtained in other polymer solvent studies there is a distinct trend with molecular weight.

This may be due to two things :-

a) The shear dependence of viscosity has been neglected and will be most apparent at high values of limiting viscosity number.

b) The polydispersity of the fractions may not be uniform. It was not considered worthwhile to use the experimental values of polydispersity since at best only an approximate value can be obtained from light-scattering data.

4. The variation in the values of ν obtained by various methods is noteworthy and points to the fact that, while in principle the calculations underlying these are correct, the assumptions made together with experimental difficulties encountered render the interpretation of results rather difficult.

5. Some controversy exists at the moment concerning the degradation of poly-4-vinyl pyridine in solution at normal temperatures. In this study no diminution in molecular weight was observed if a solution was left in a closed flask for c a. 14 days before measurements. On raising the temperature of solutions in sealed tubes to 100°C, however, a marked decrease in scatter was observed indicating considerable degradation.

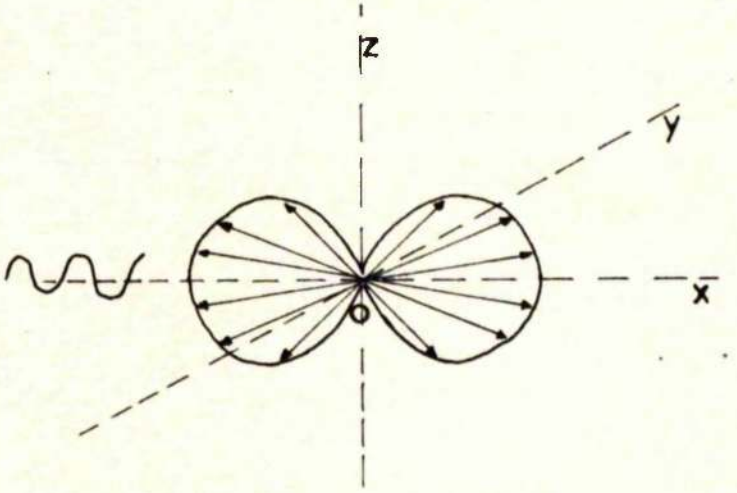


Fig. 1 Angular Dependence of Scatter for Polarised Light.

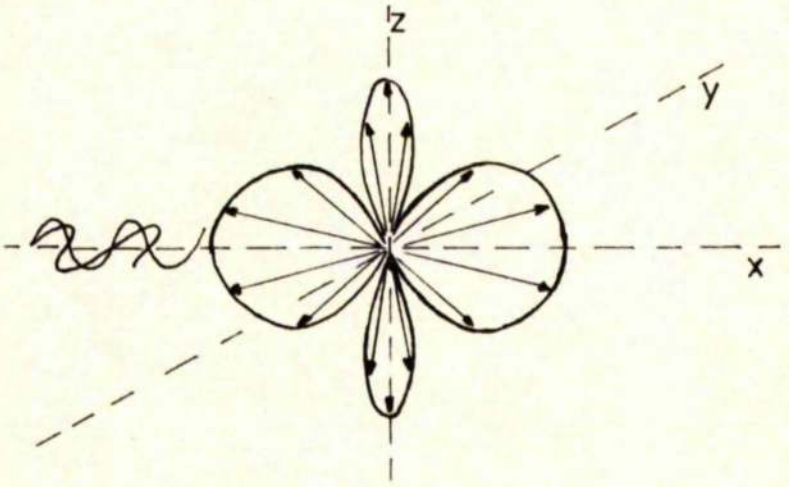


Fig. 2 Angular Dependence of Scatter for Unpolarised Light.

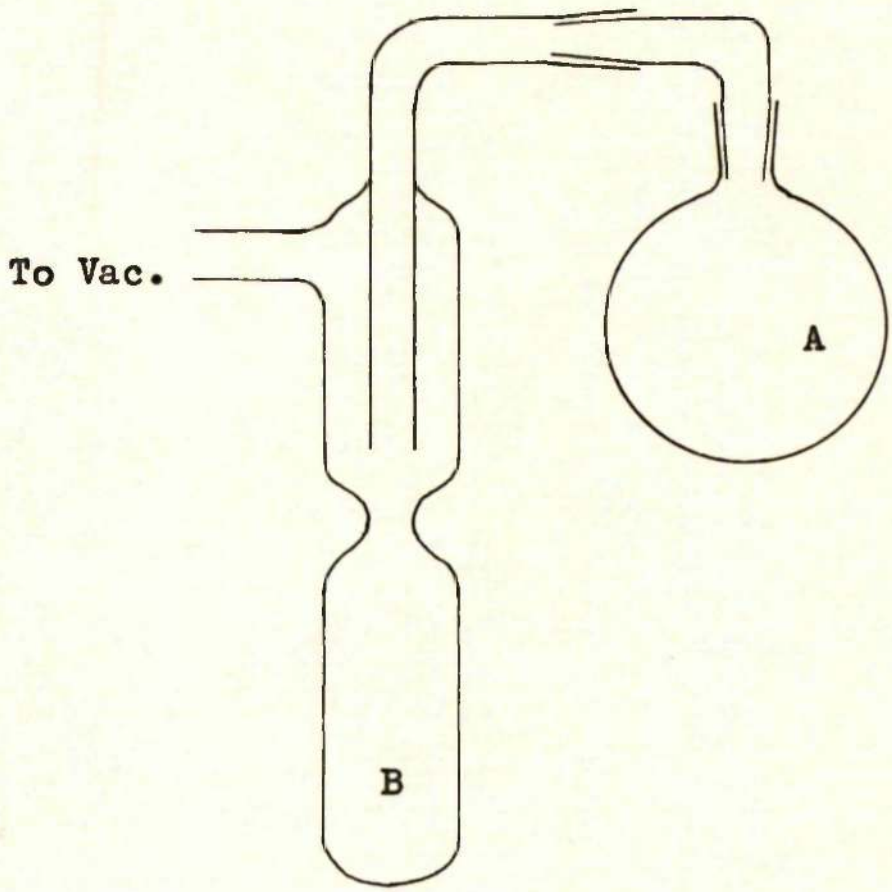


Fig.3 Polymerisation Apparatus

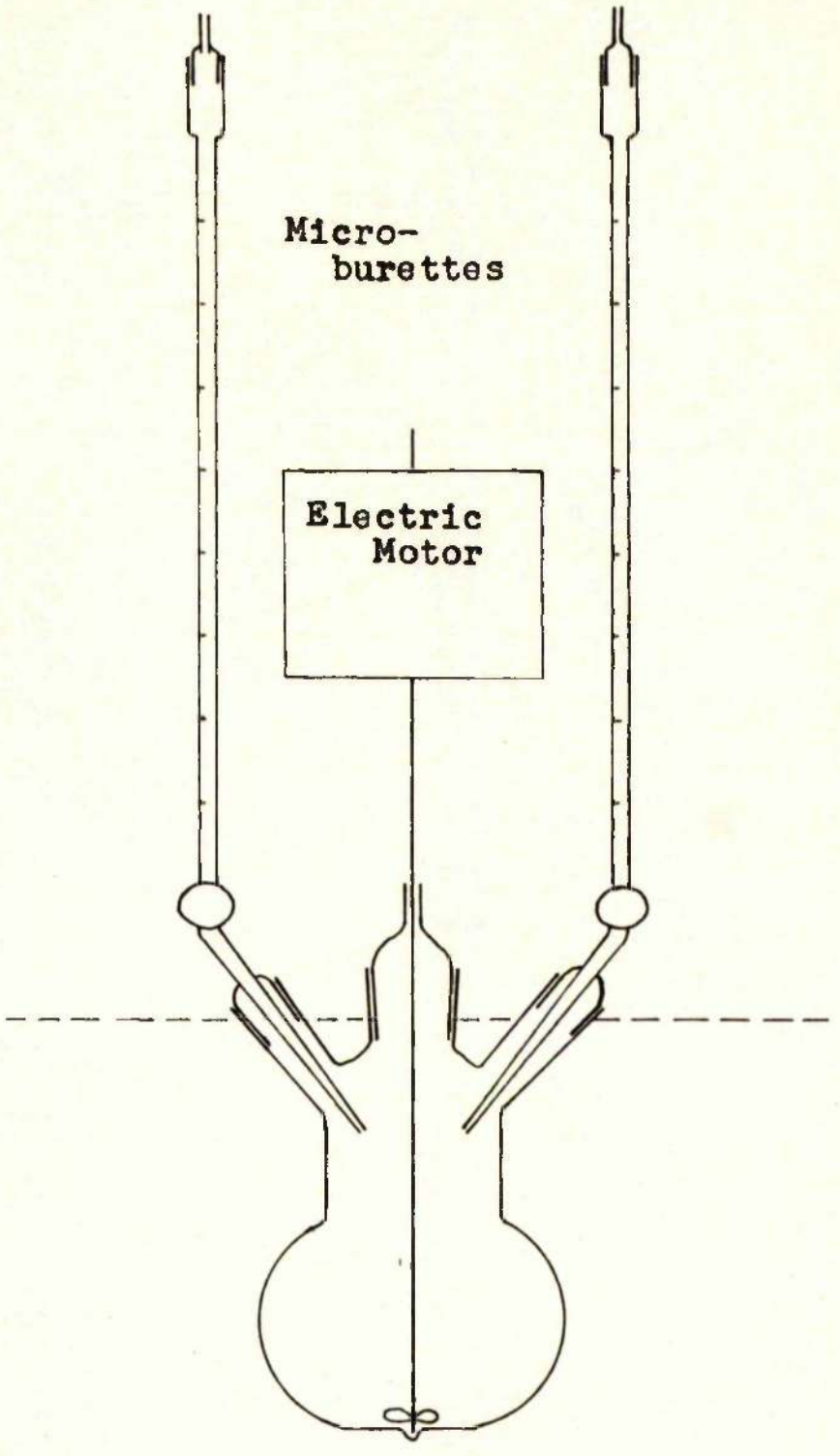


Fig.4 Apparatus for Determination of θ-solvent Composition

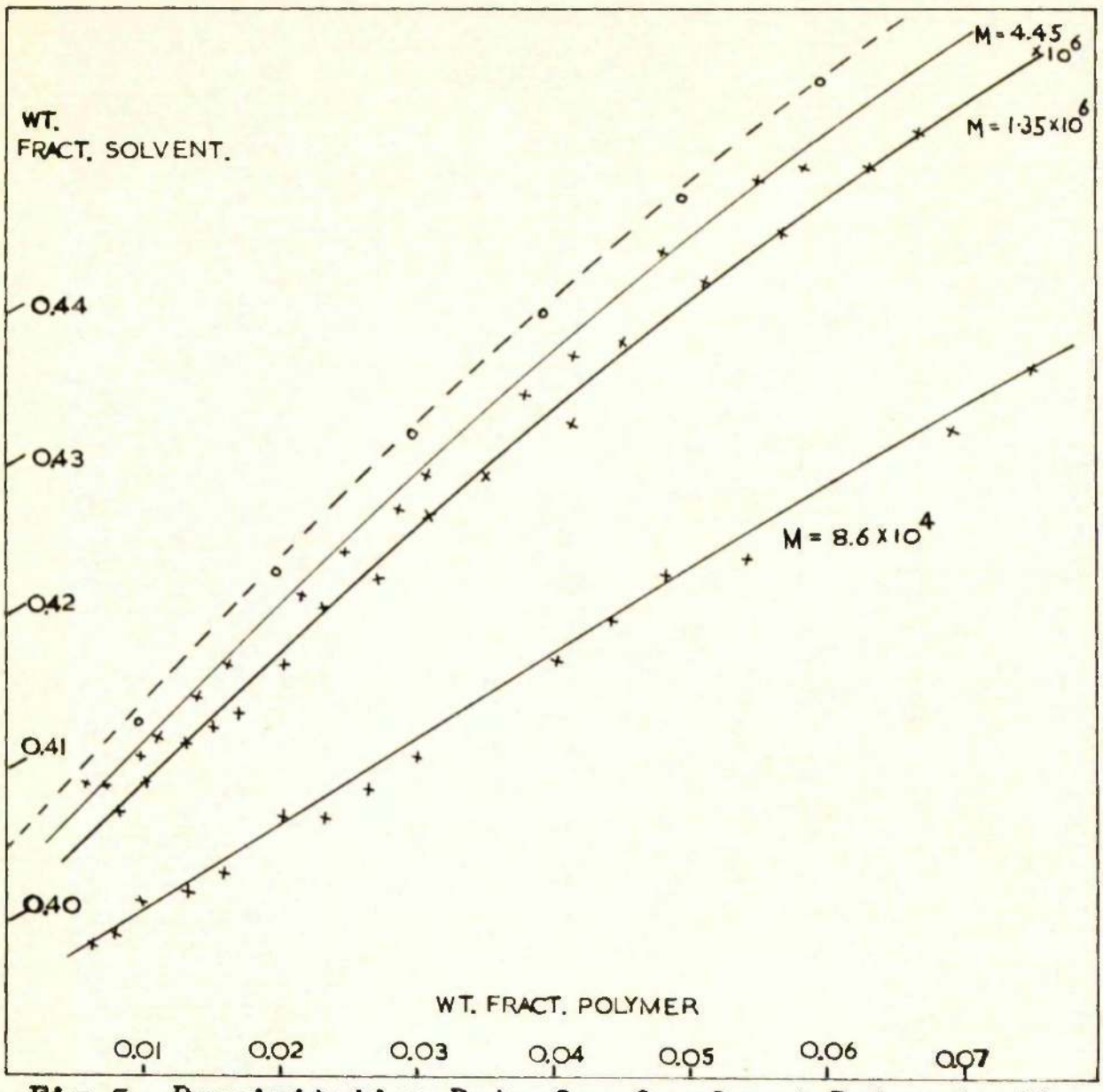


Fig.5 Precipitation Data for θ-solvent Determination

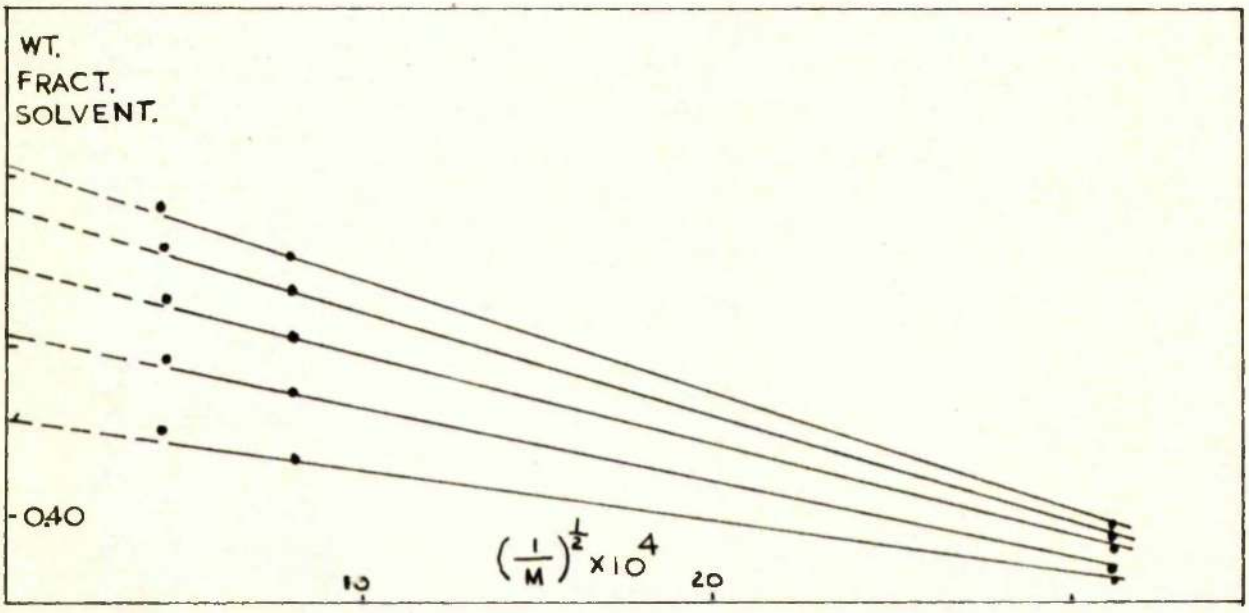


Fig.6 Extrapolation of θ-solvent Data to M=∞

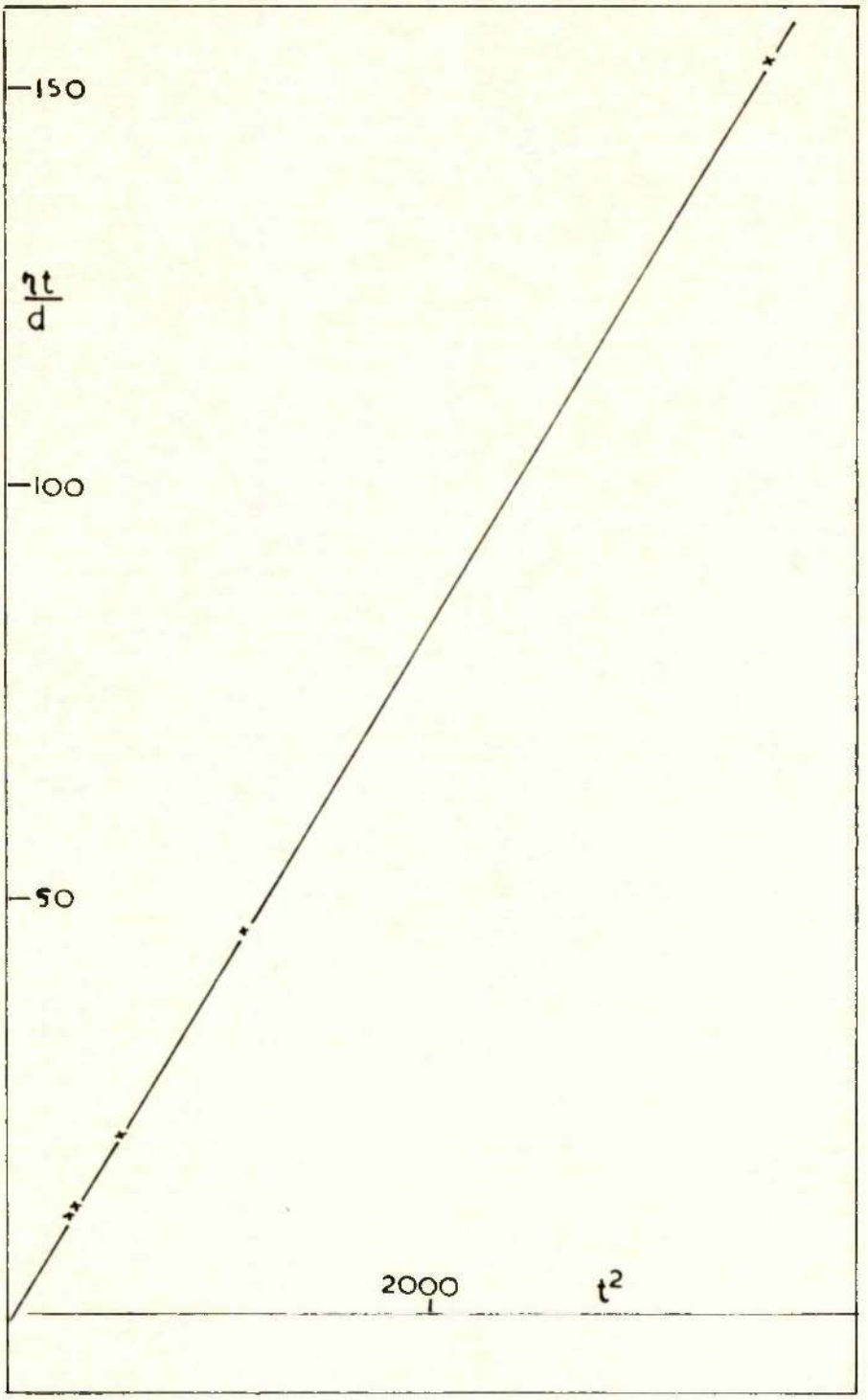


Fig.7 Calibration Plot for Viscometer Kinetic Energy Correction

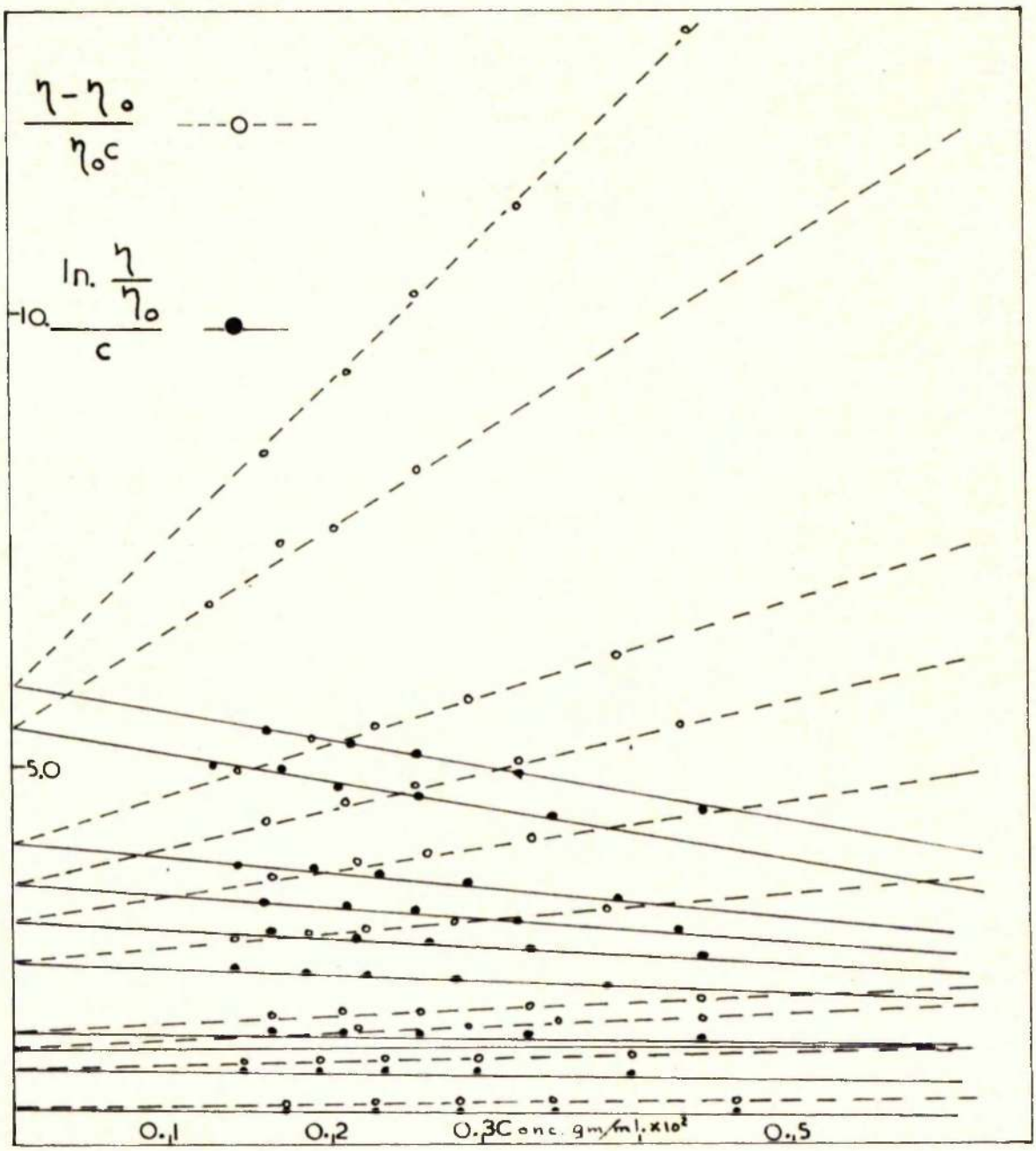


Fig.8 Viscosity Results in Ethanol

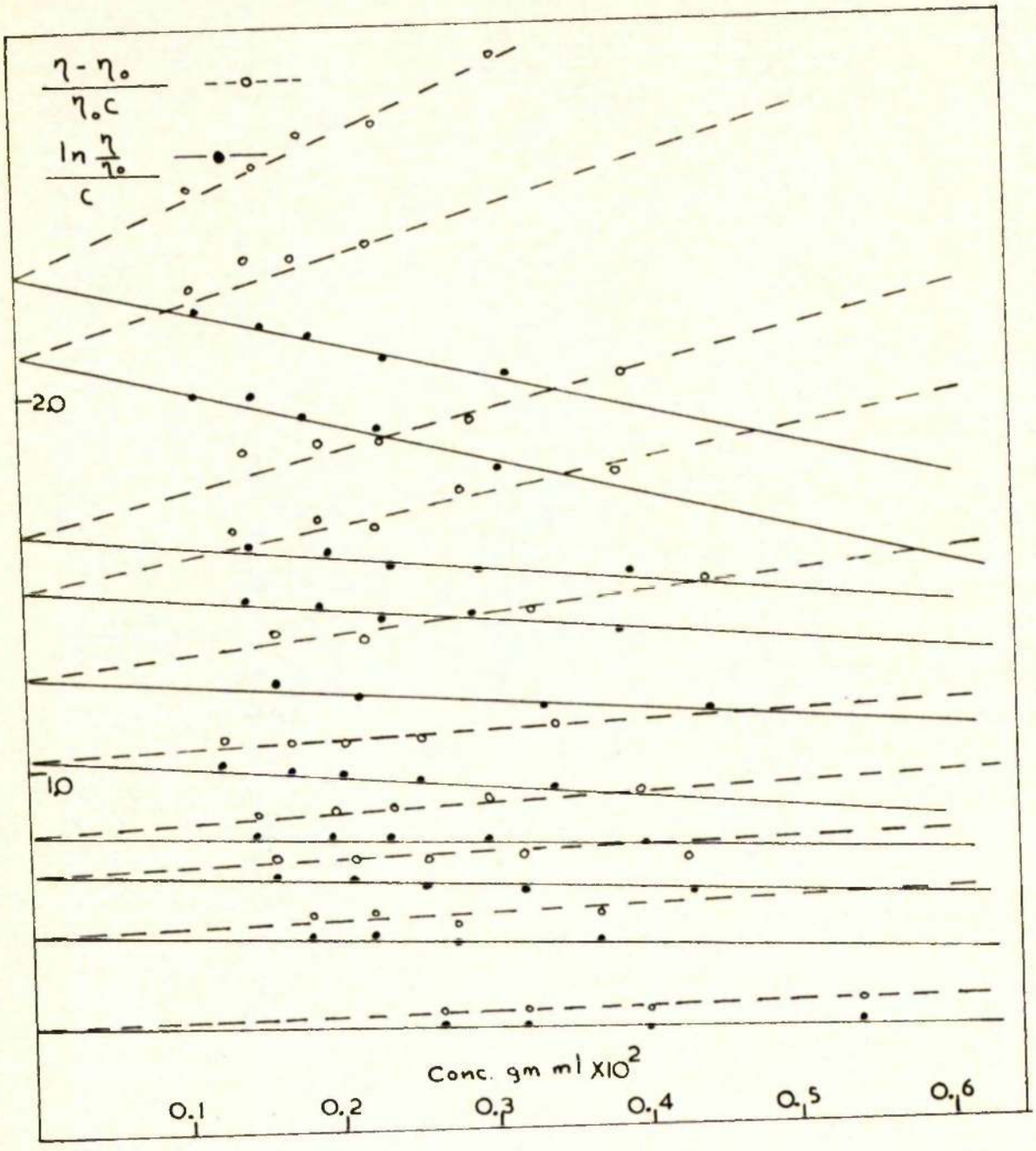


Fig.9 Viscosity Results in θ-solvent

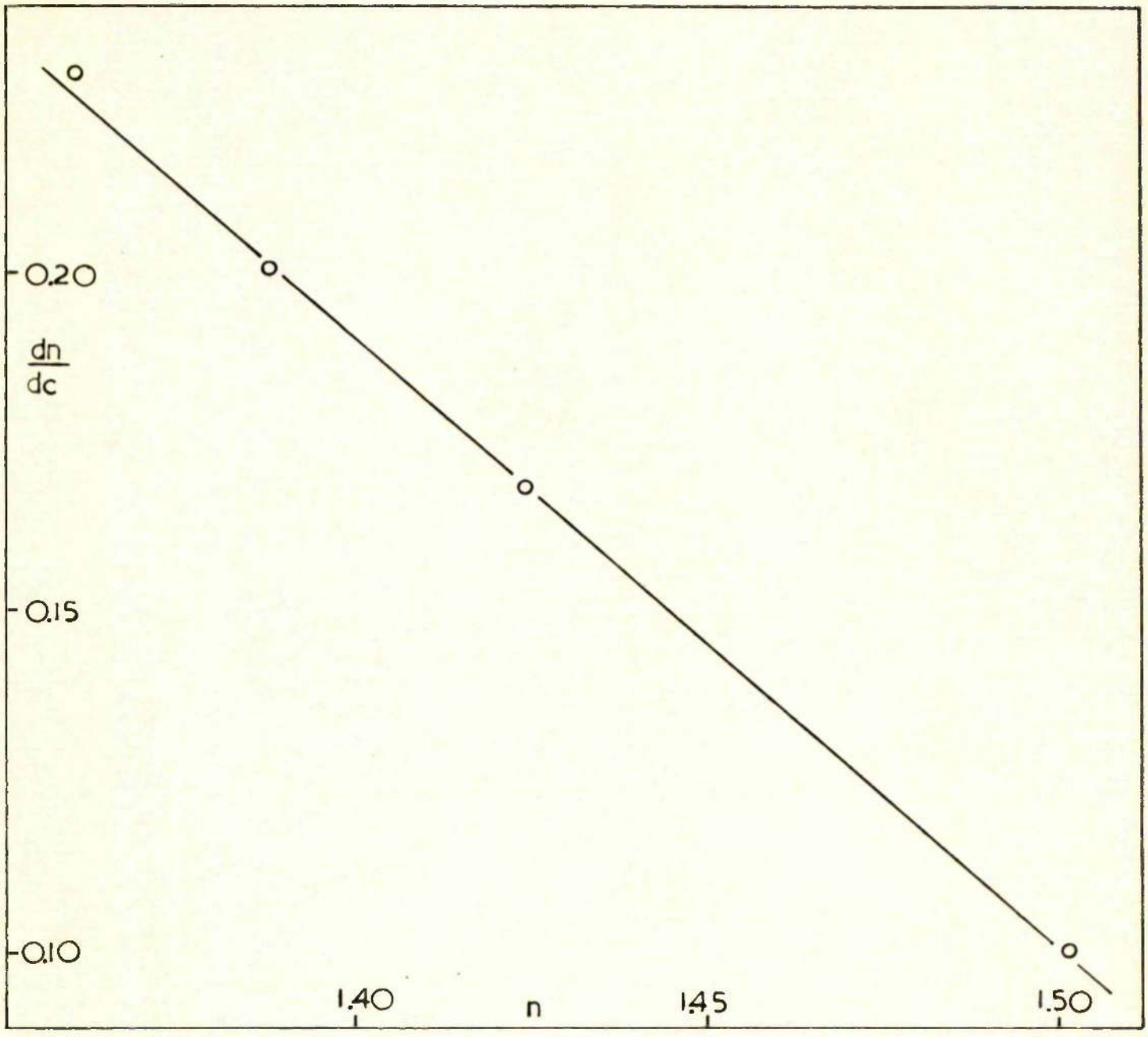


Fig.10 Plot of Gladstone and Dale Relationship

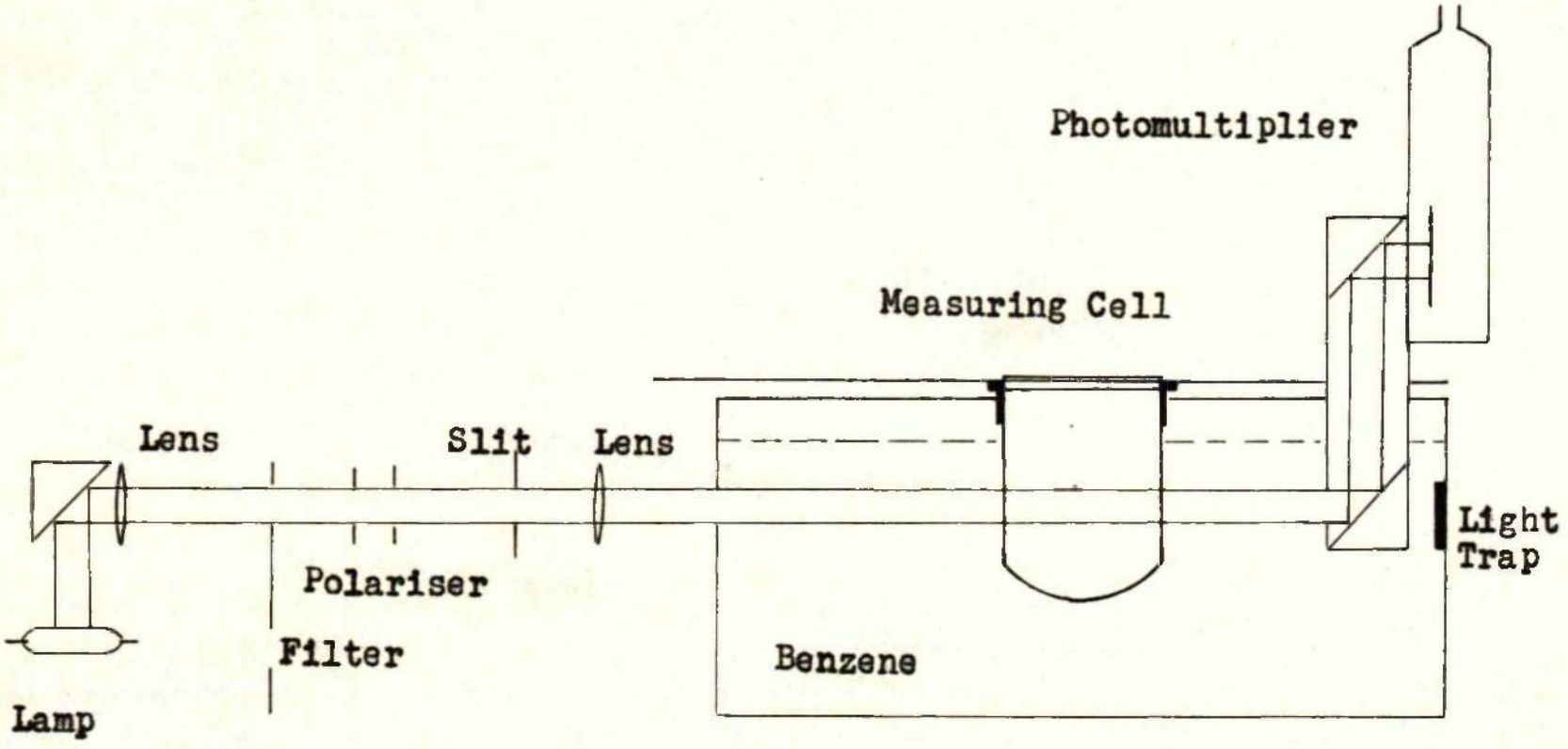


Fig.11 Light-Scattering Apparatus

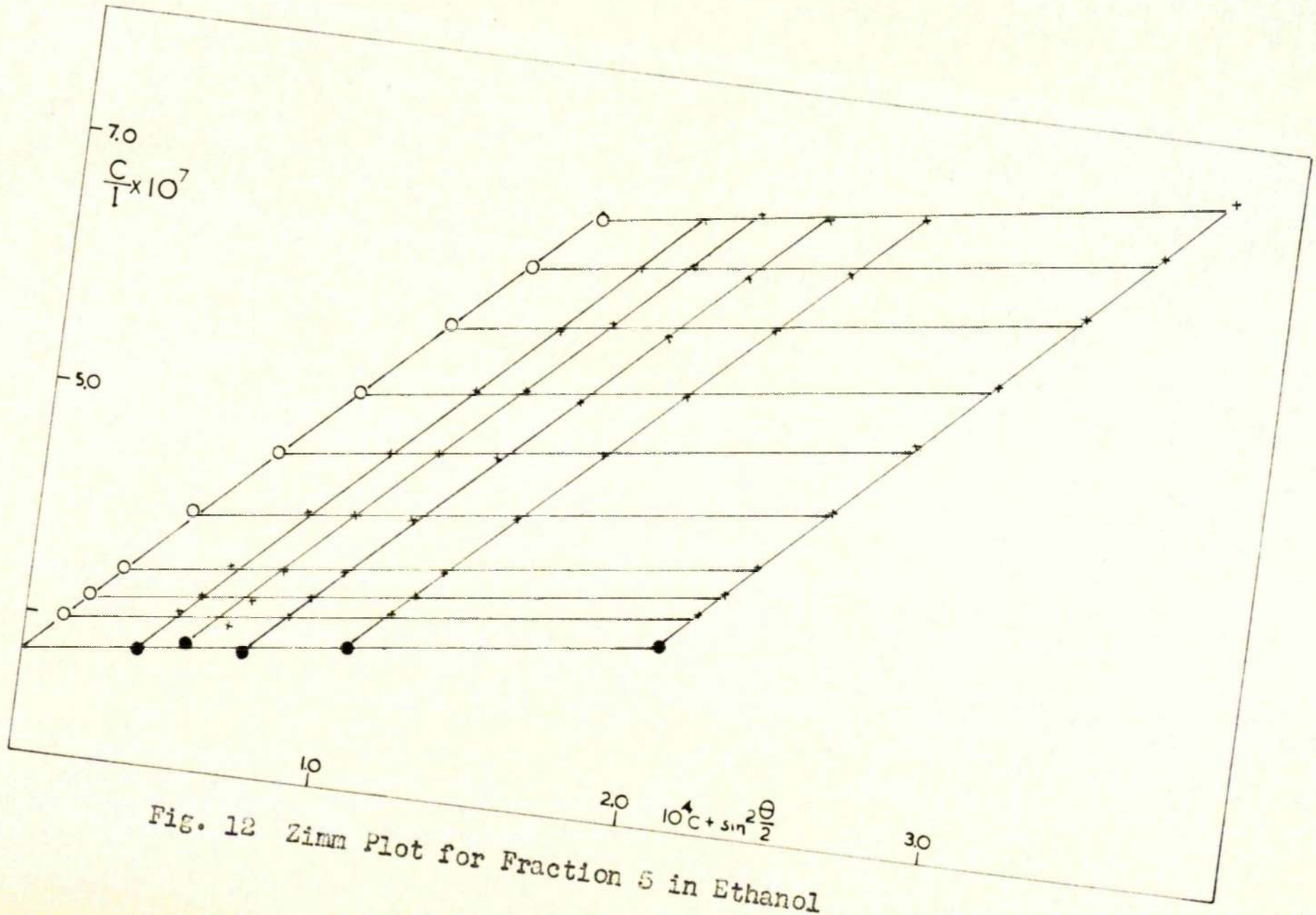


Fig. 12 Zimm Plot for Fraction 5 in Ethanol

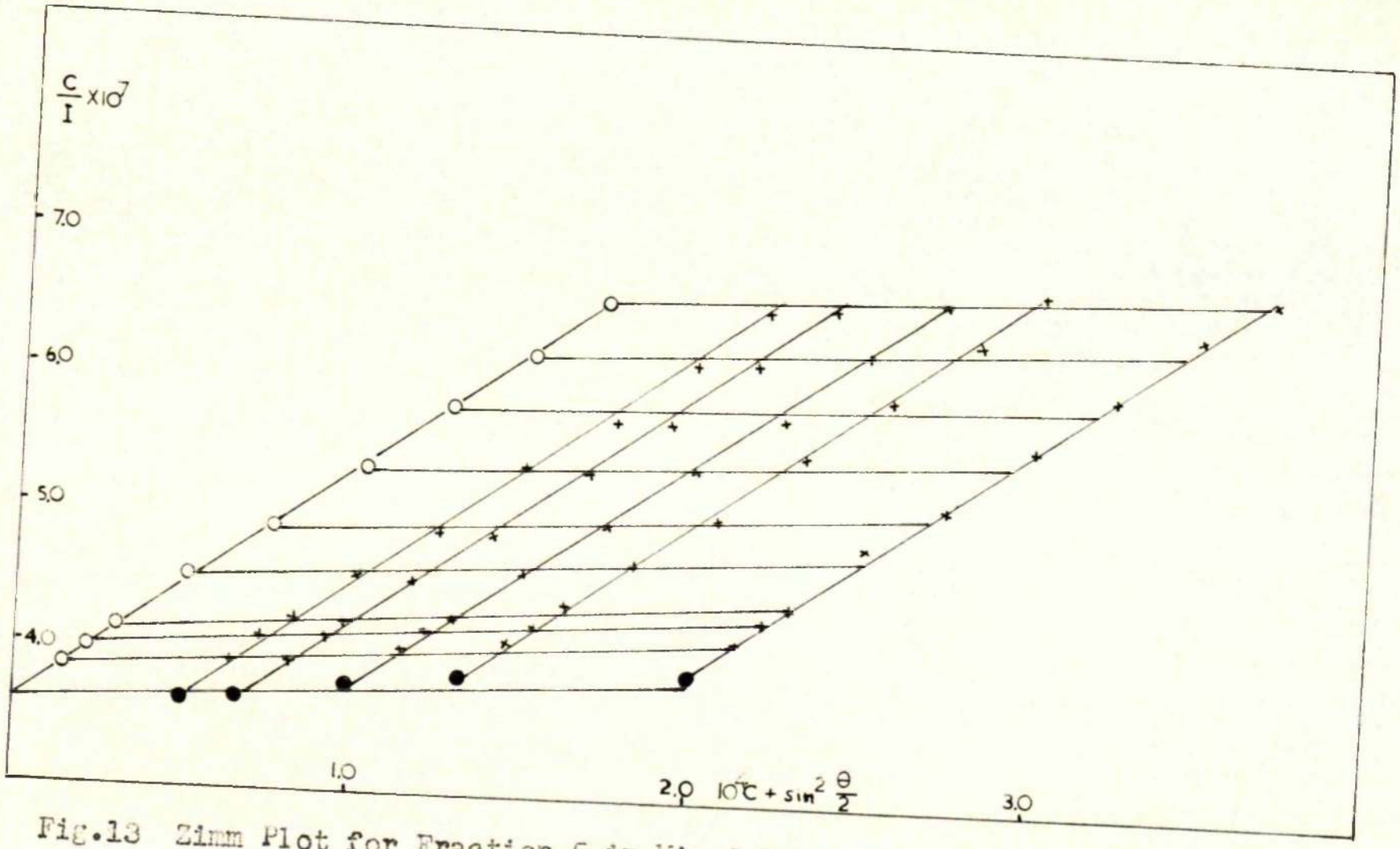


Fig.13 Zimm Plot for Fraction 5 in Mixed Solvent

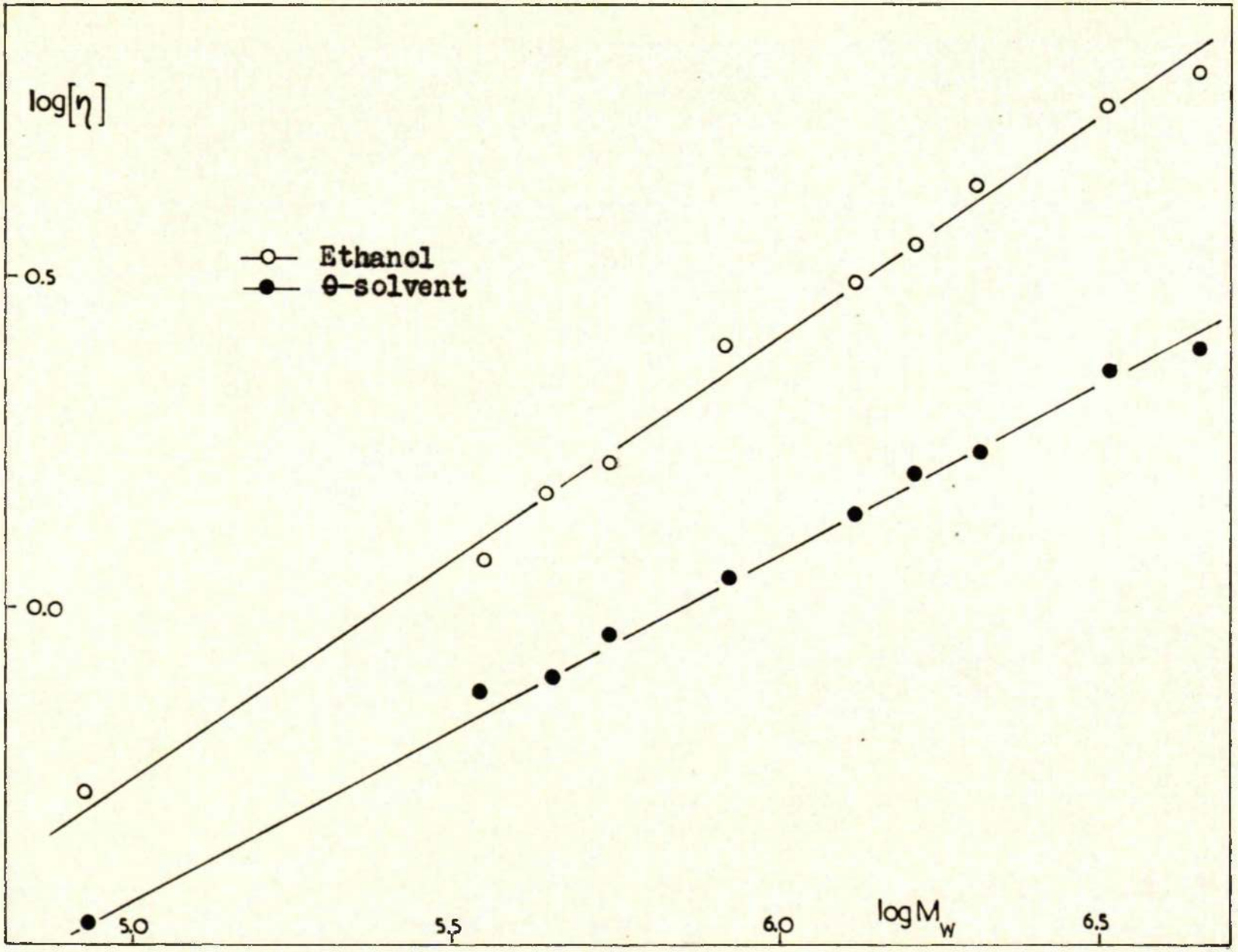


Fig.14 Plots of Mark-Houwink Equation in Two Solvents

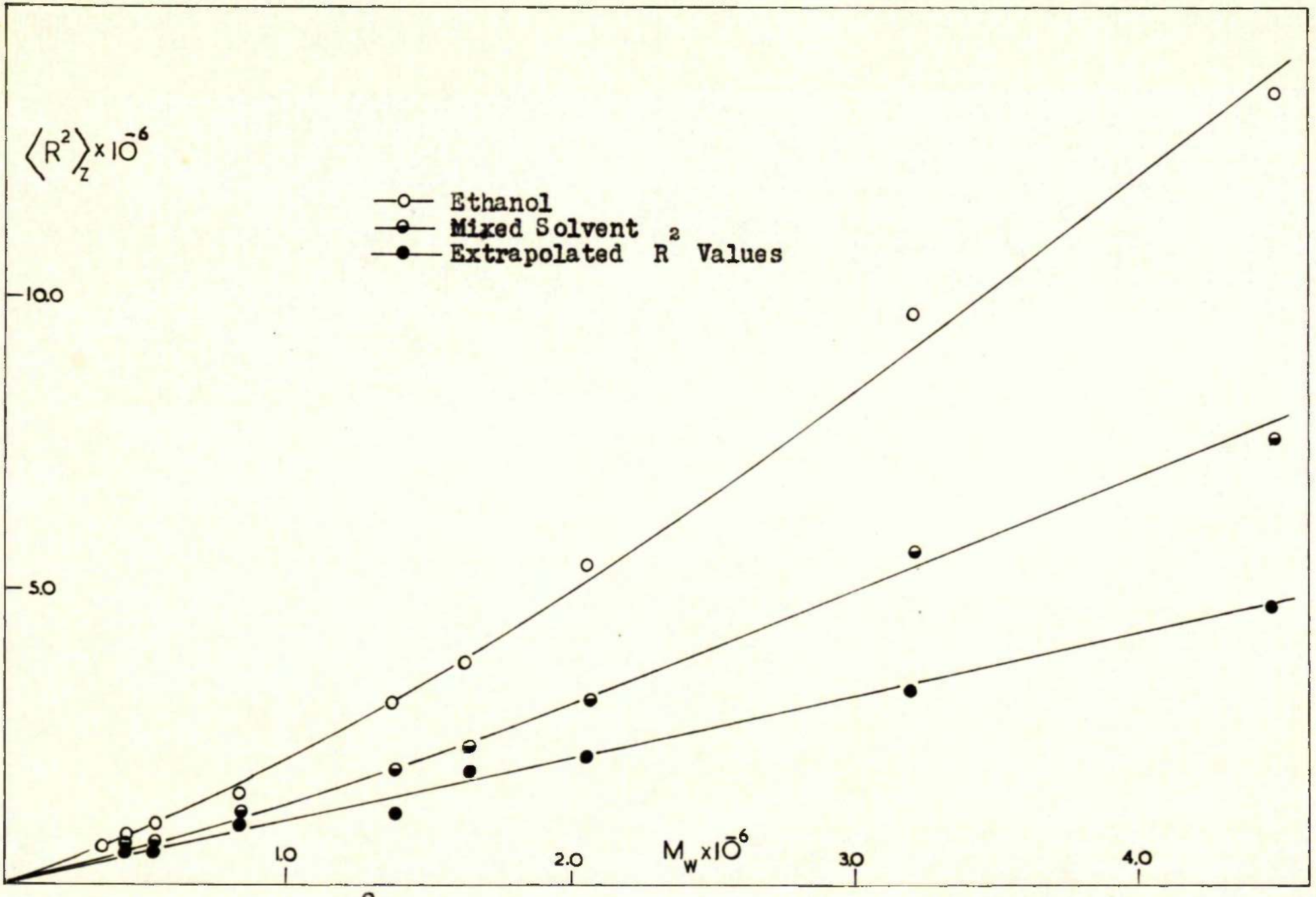


Fig.15 Plots of $\langle R^2 \rangle_z$ – Mw Relationships

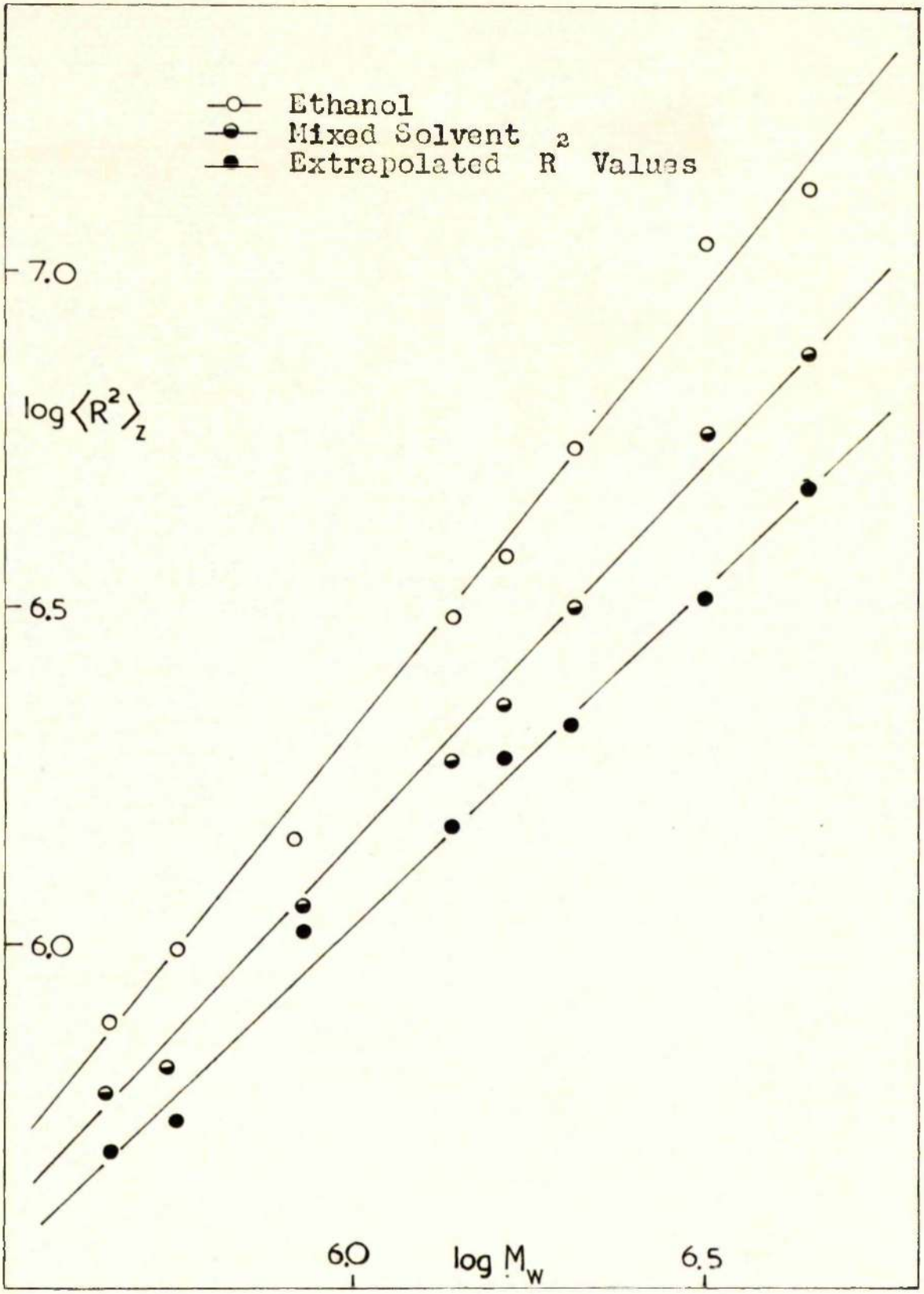


Fig.16 Logarithmic Plots of $\langle R^2 \rangle$-Mw Relationships

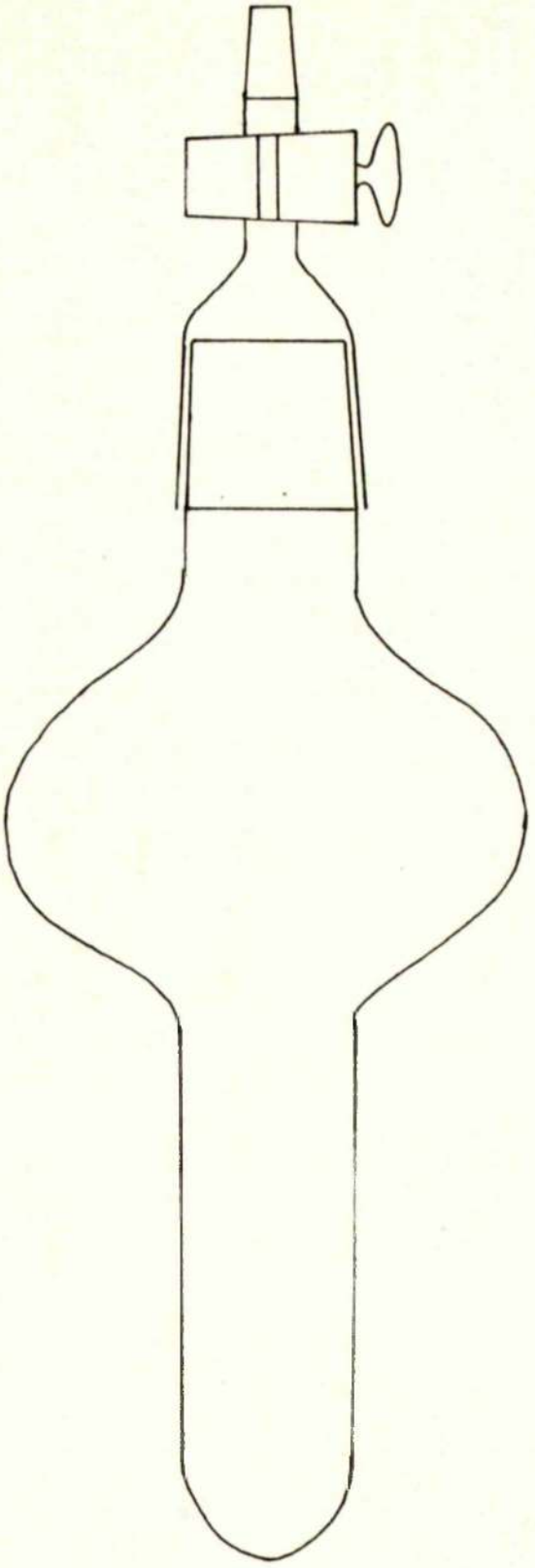


Fig.17 Light-Scattering Cell for Concentrated Polymer Solutions

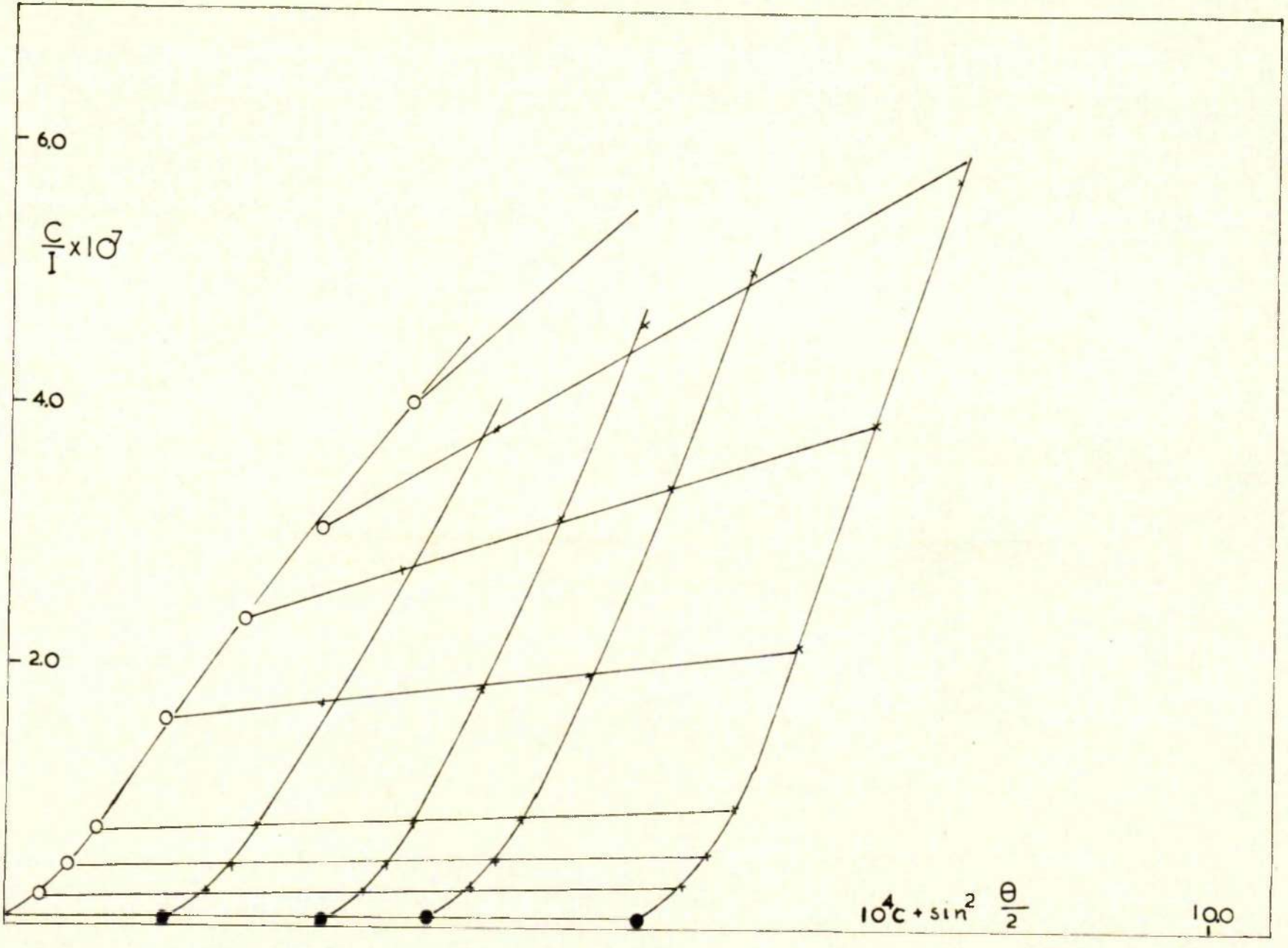


Fig.18 Zimm Plot for P.E.1 in Water

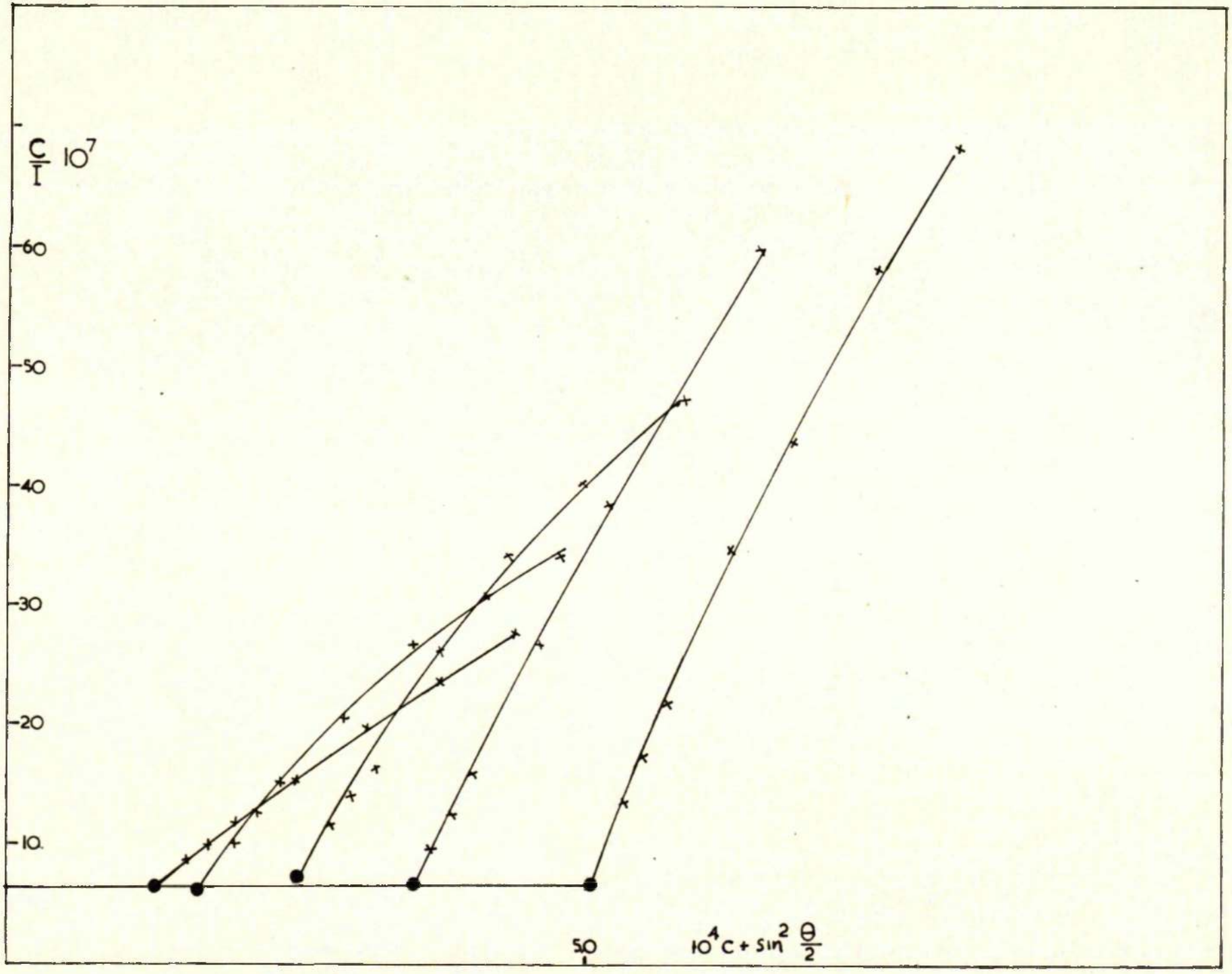


Fig. 19 Zimm Plot for P.E.1 in Methanol

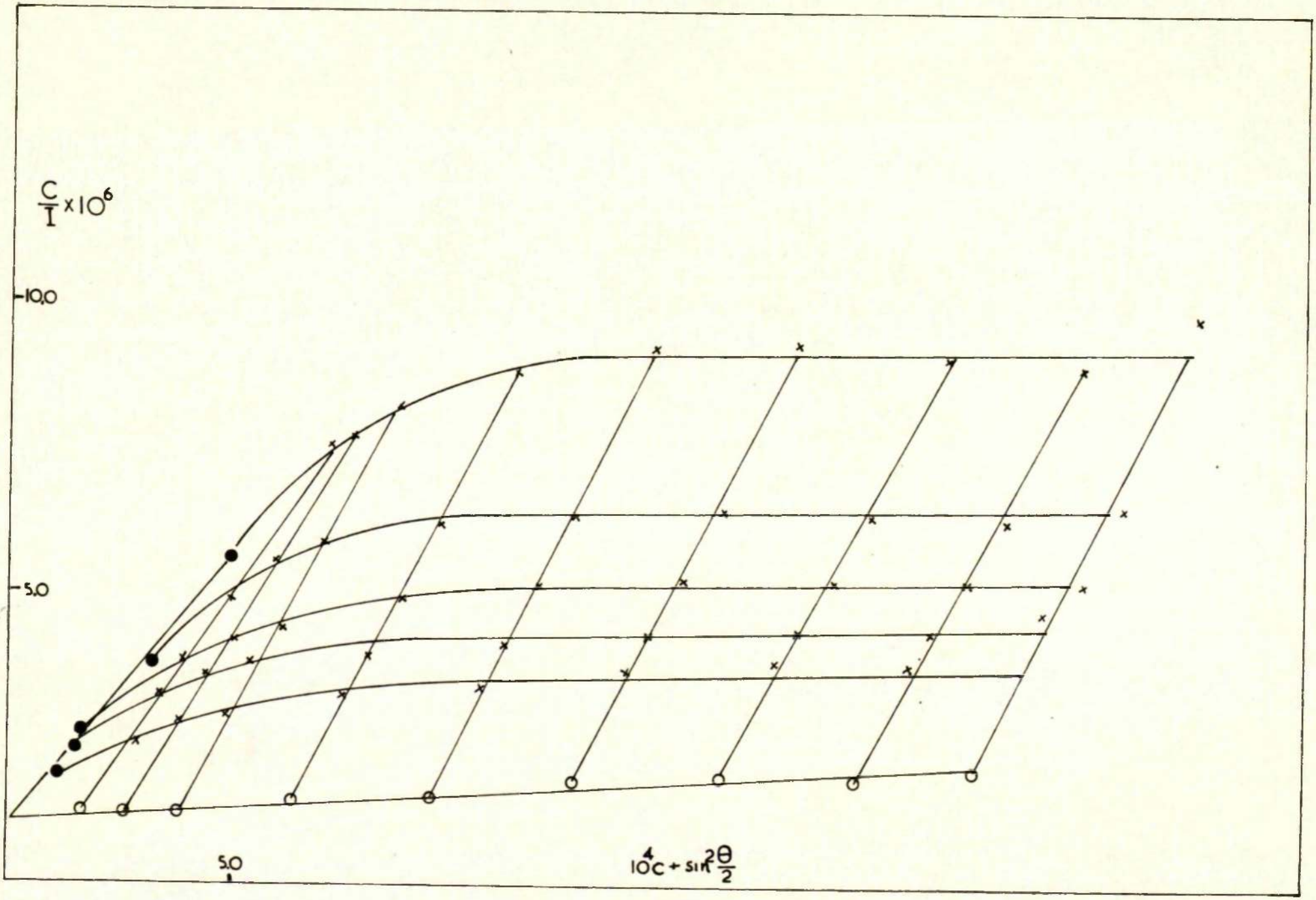


Fig. 20 Zimm Plot for P.E.1 in Ethanol

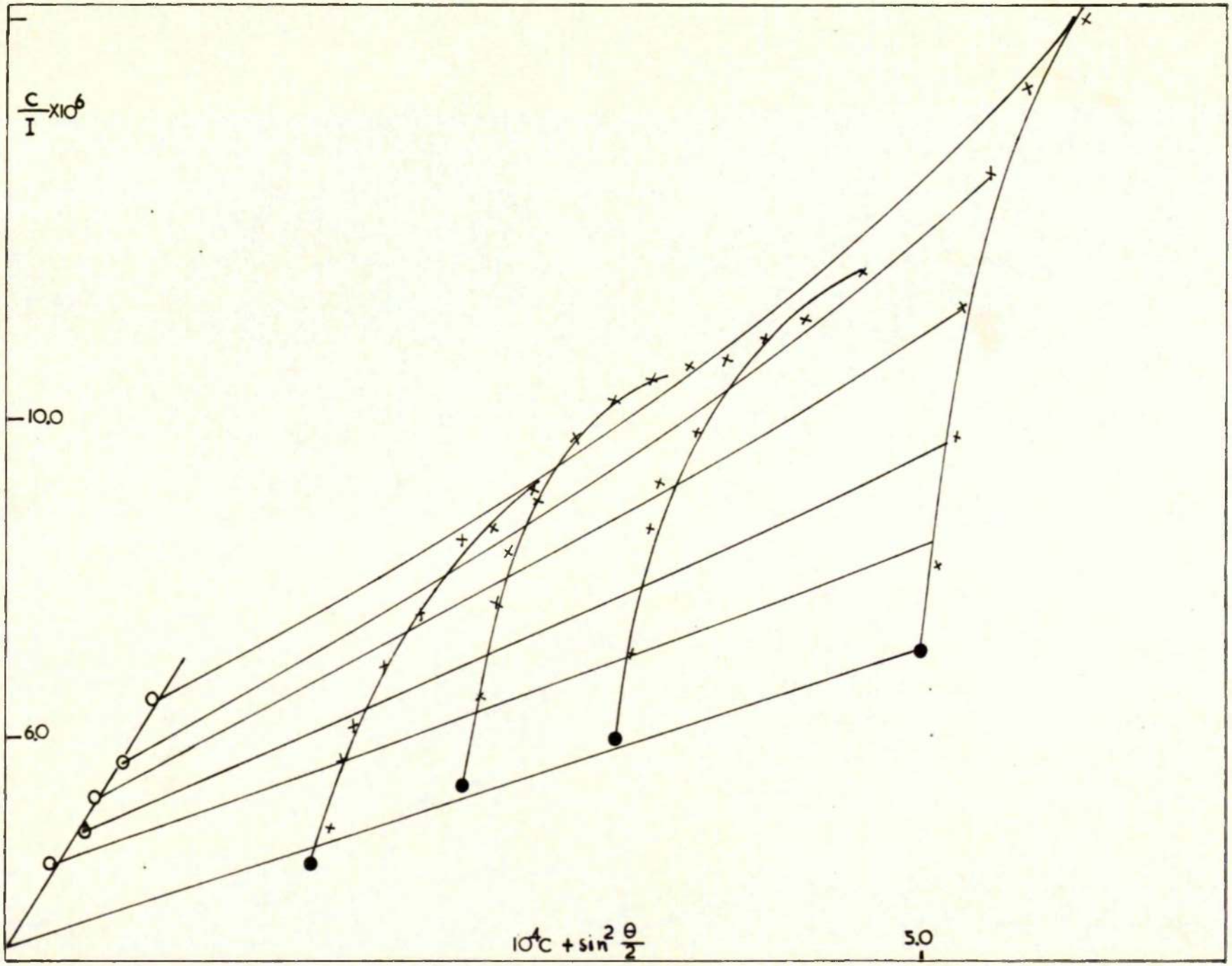


Fig.21 Zimm Plot for P.E.1 in Dimethylformamide

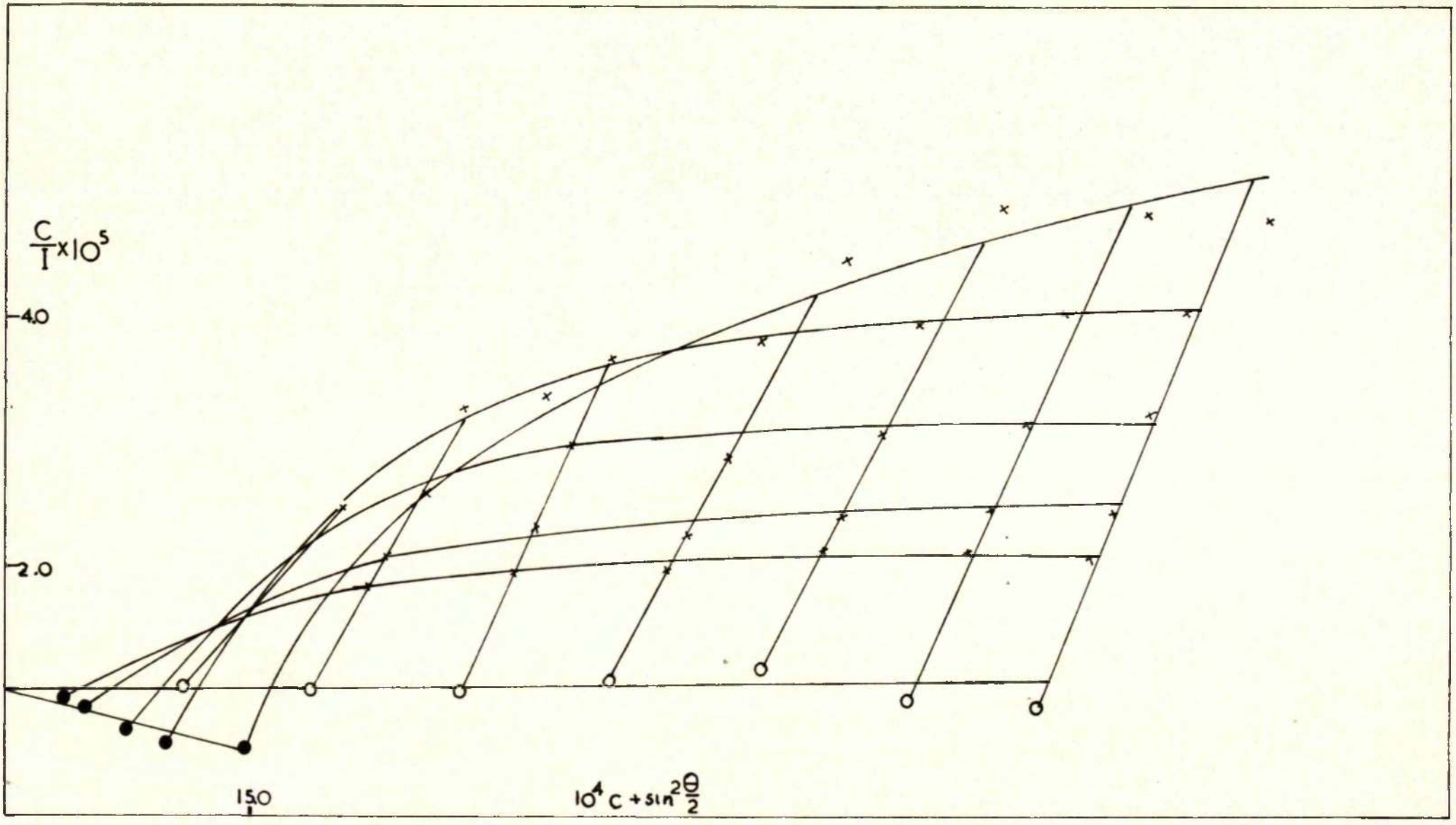


Fig. 22 Zimm Plot for P.E.1 in Dimethylsulphoxide

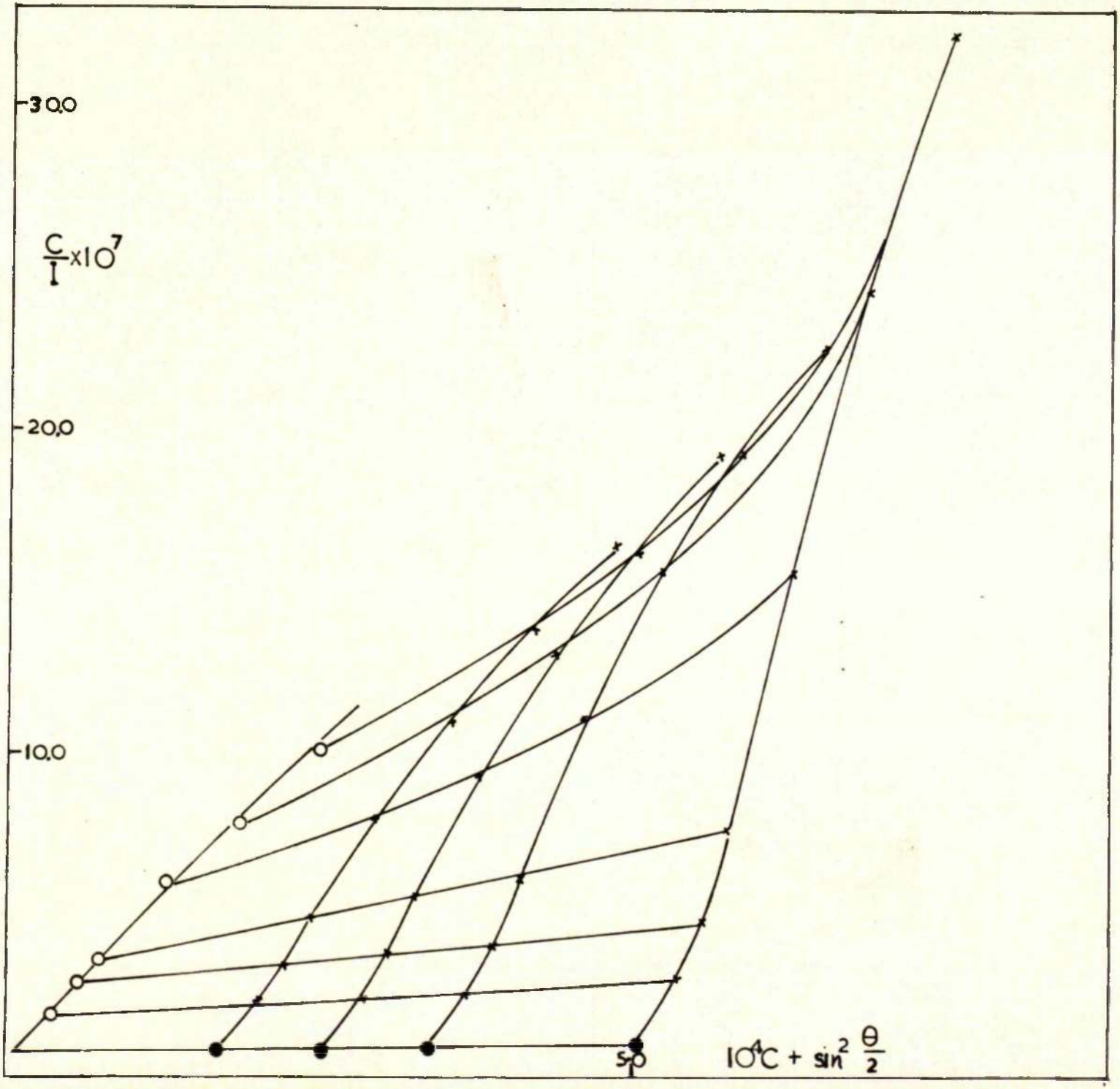


Fig. 23 Zimm Plot for P.E.1 in 0.0075 M. KBr

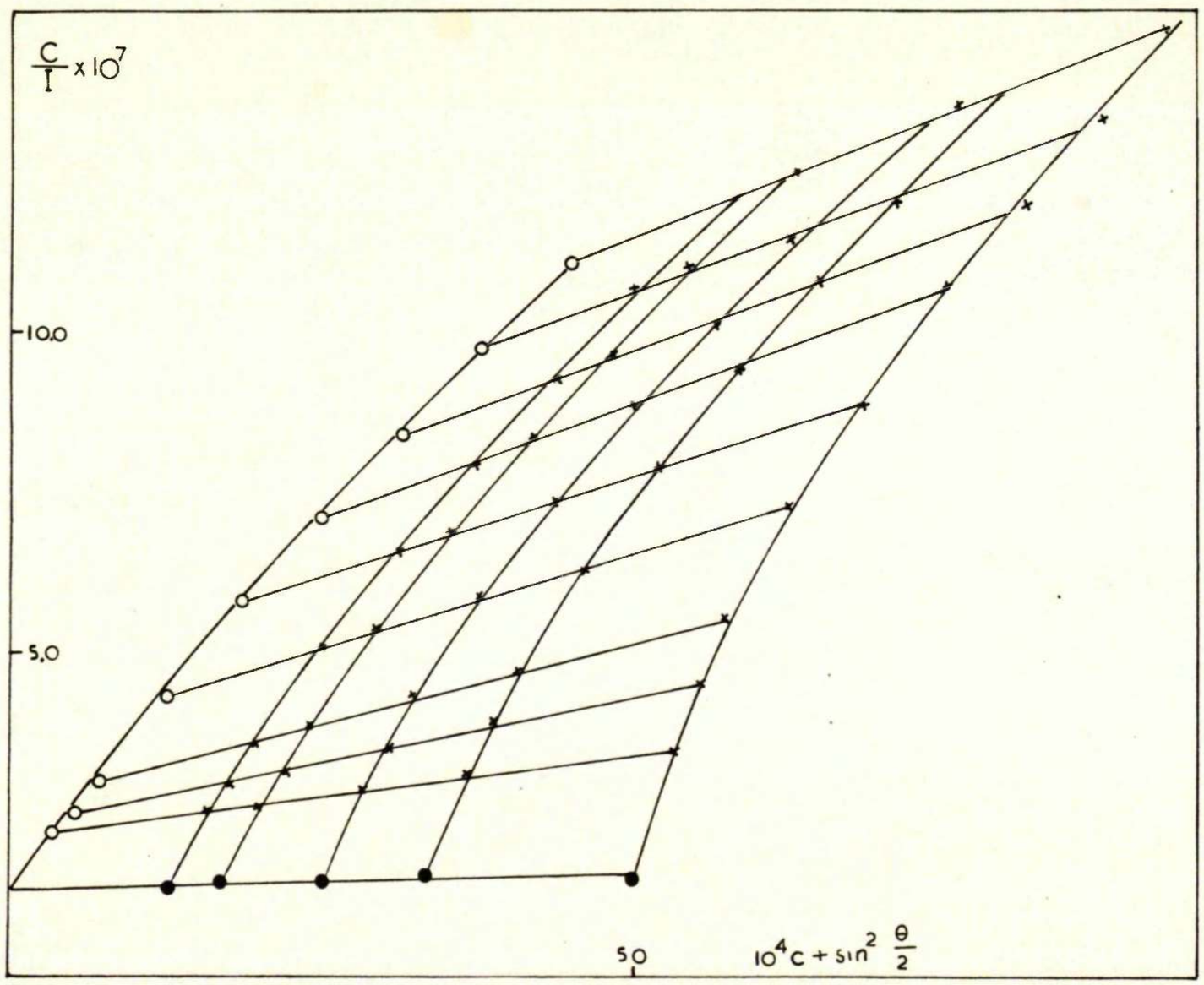


Fig.24 Zimm Plot for P.S. 1 in 0.05 M. KBr.

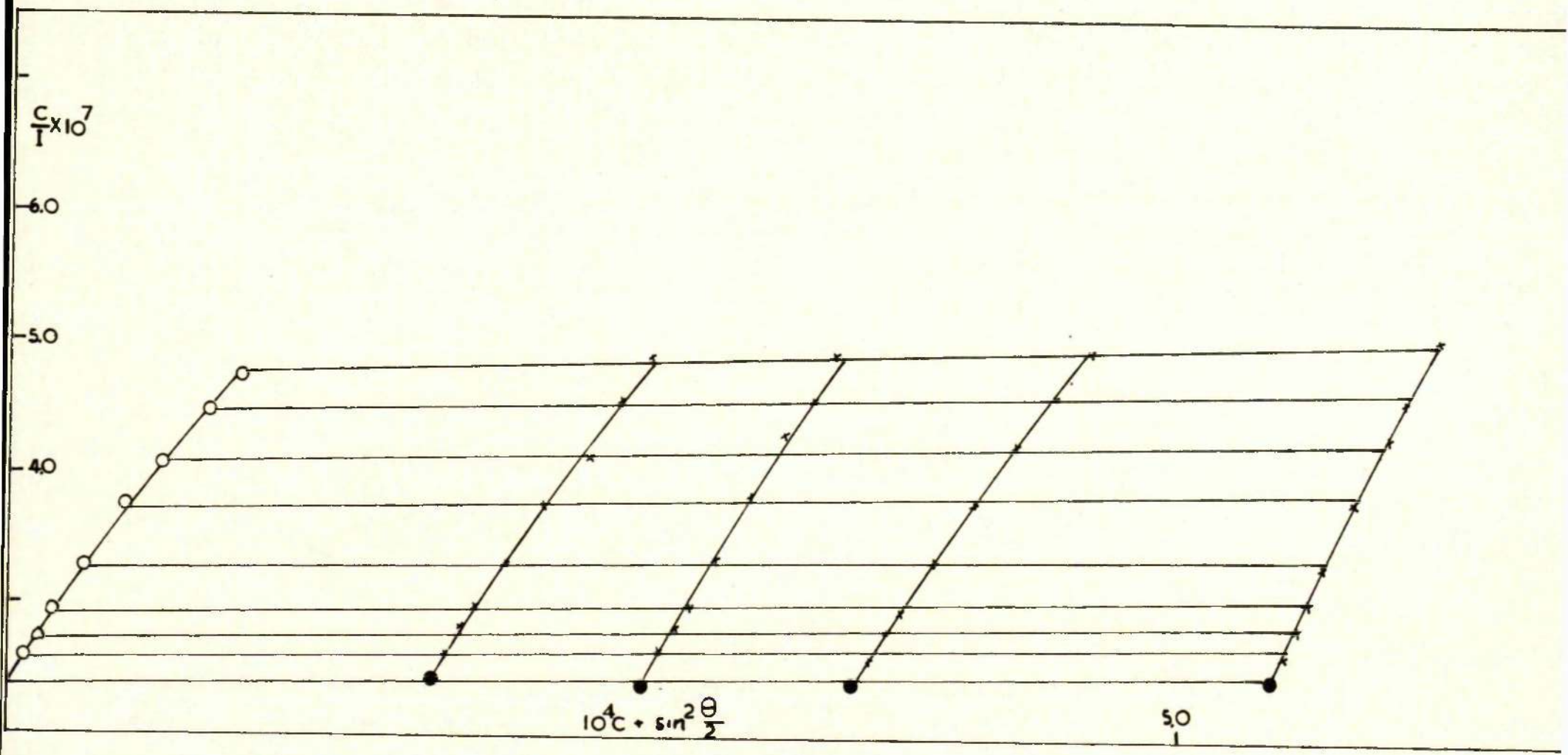


Fig.25 Zimm Plot for P.E.1 in 0.4 M. KBr

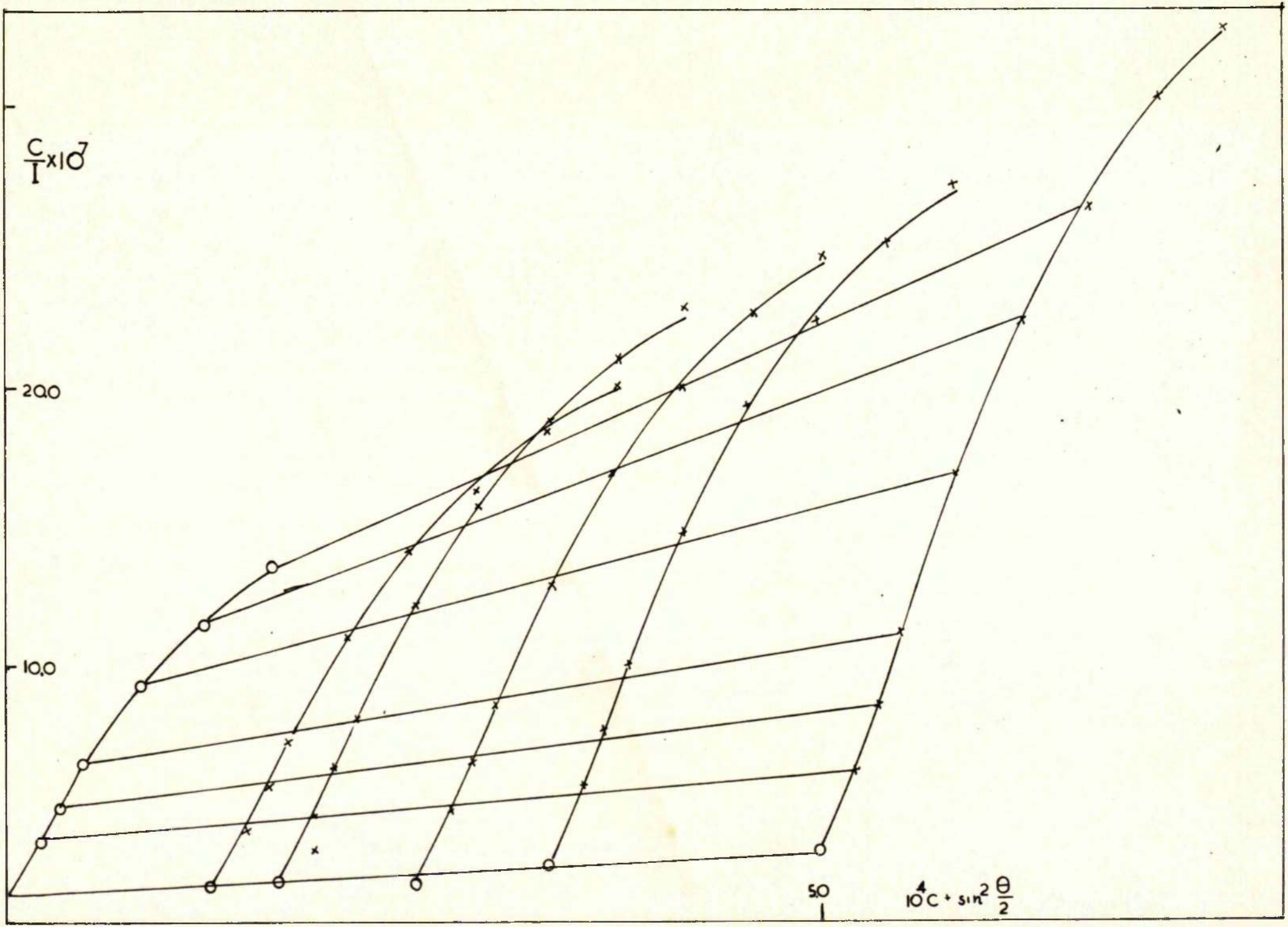


Fig.26 Zimm Plot for P.E.2 in 0.0075 M. KBr

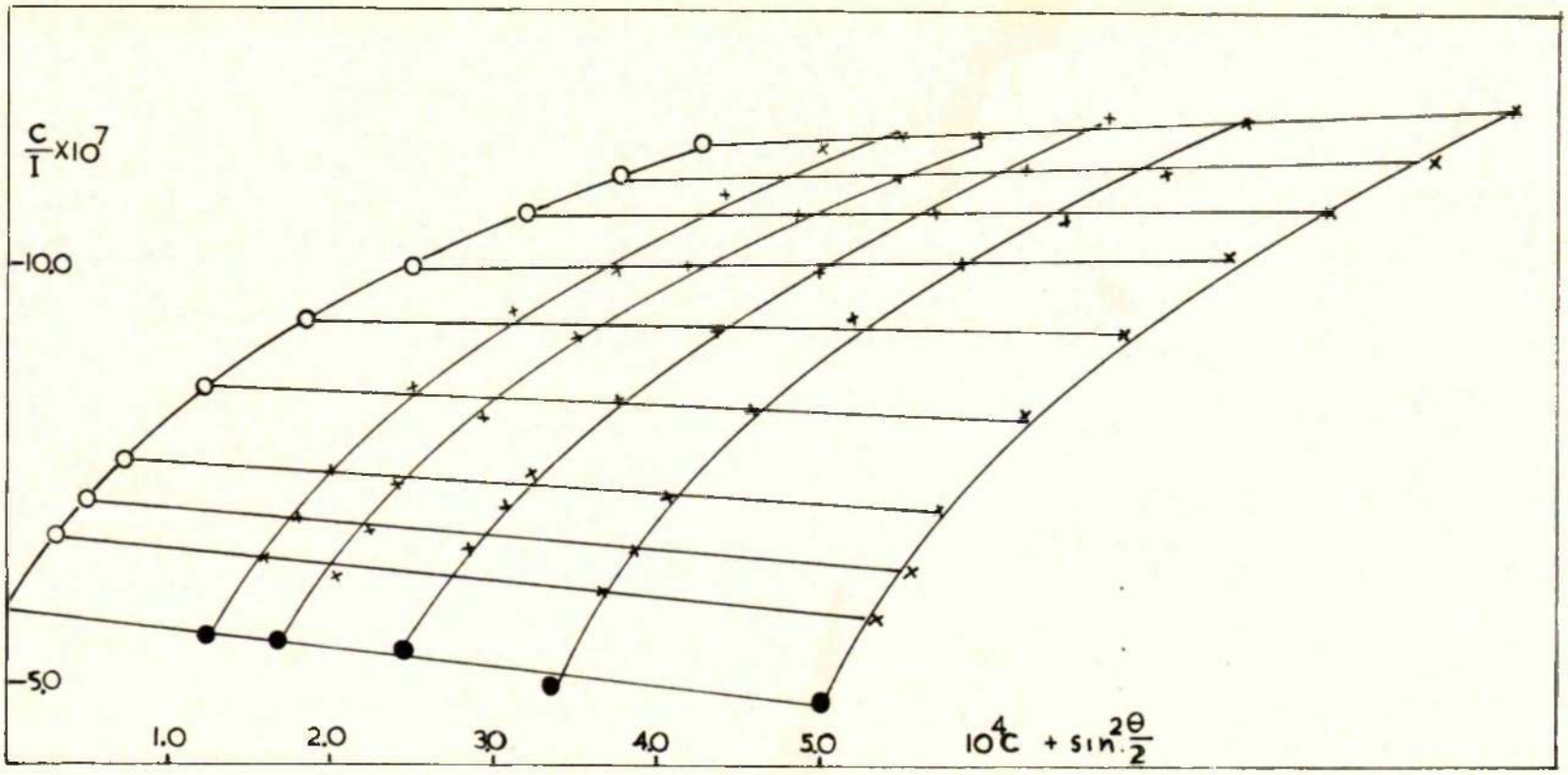


Fig.27 Zimm Plot for P.E.2 in 0.25 M. KBr

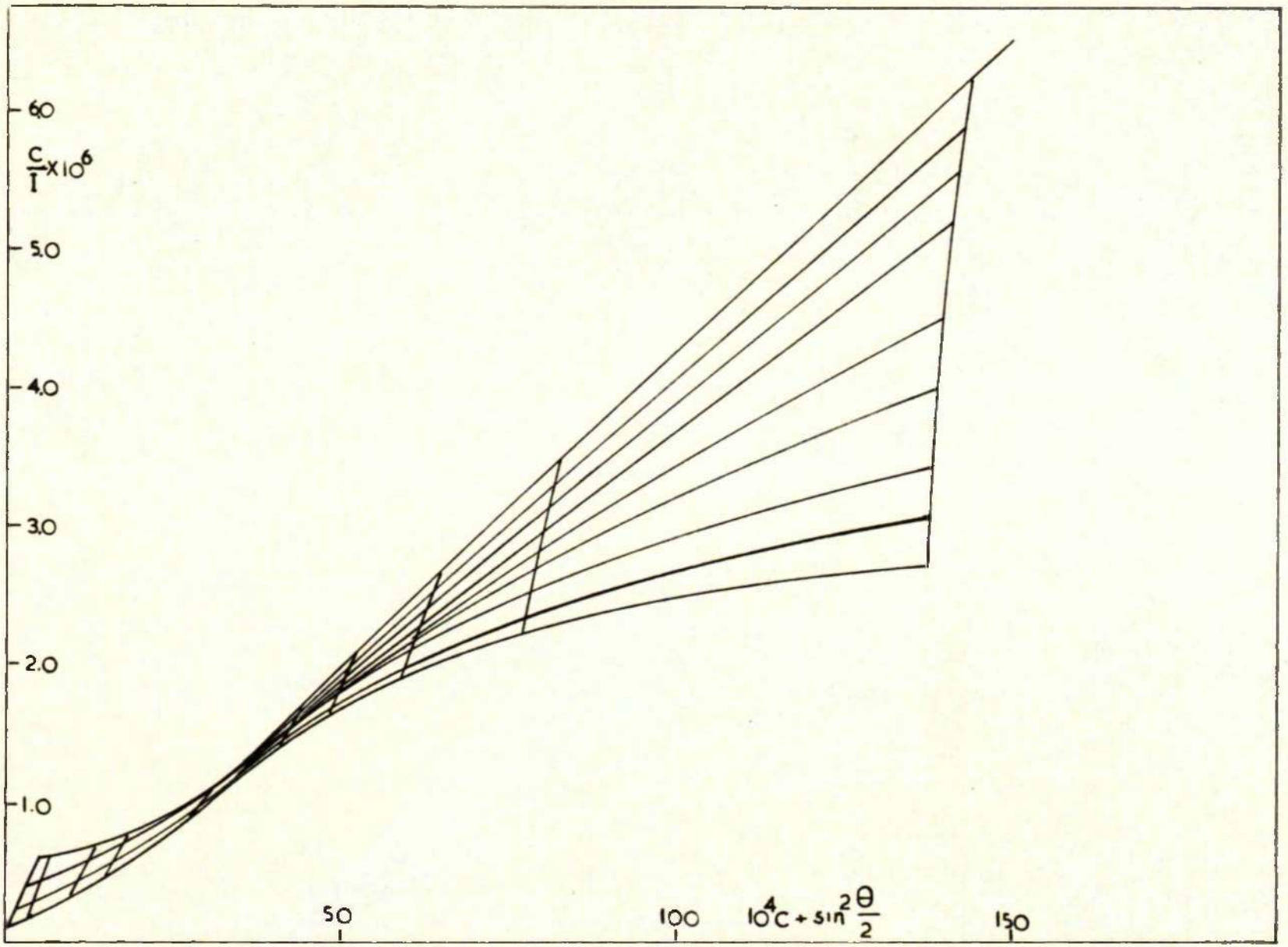


Fig.28 Zimm Plot for Polymer in Concentrated Solution (Fraction 1)

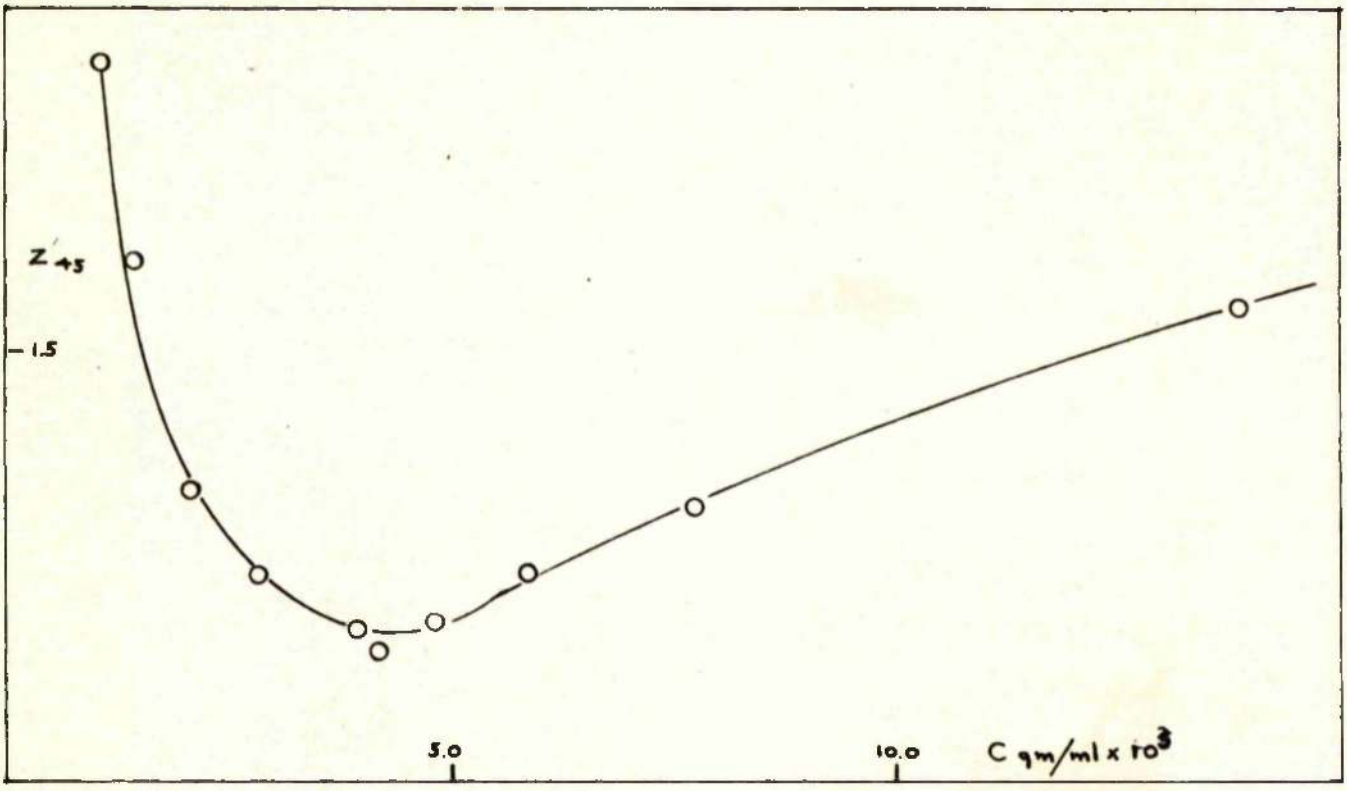


Fig.29 Plot Showing Variation of Dissymmetry z with Concentration for Uncharged Polymer

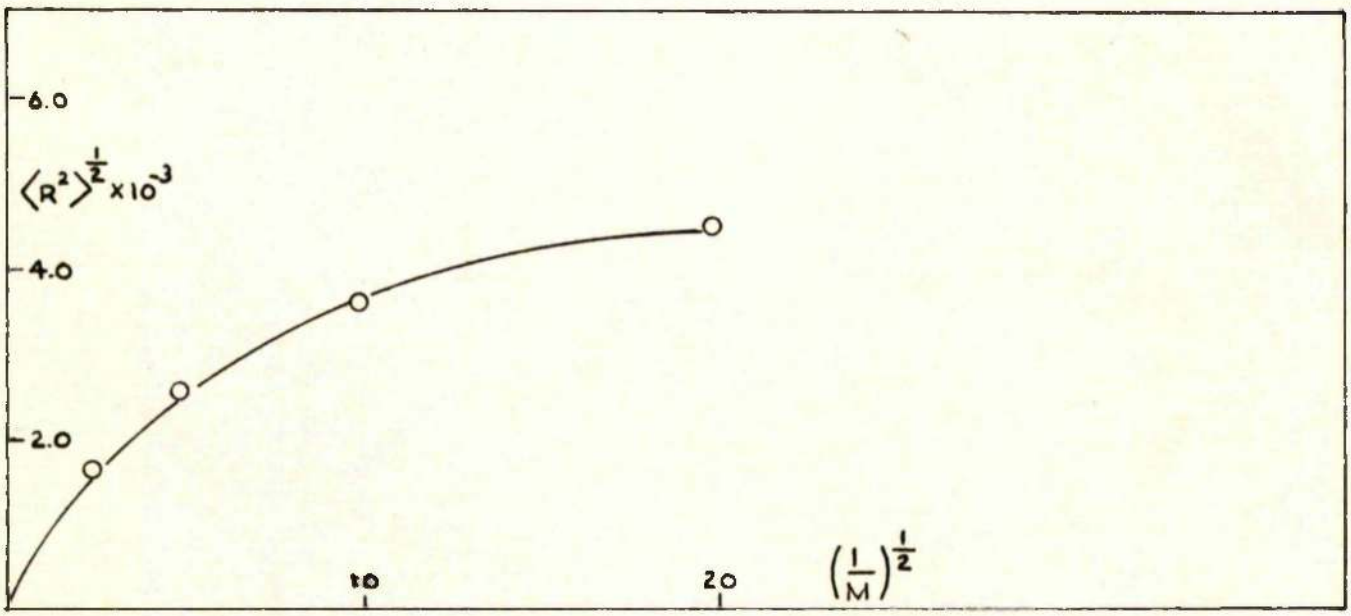


Fig.30 Extrapolation of Molecular Dimensions for P.E.1 to Infinite Ionic Strength

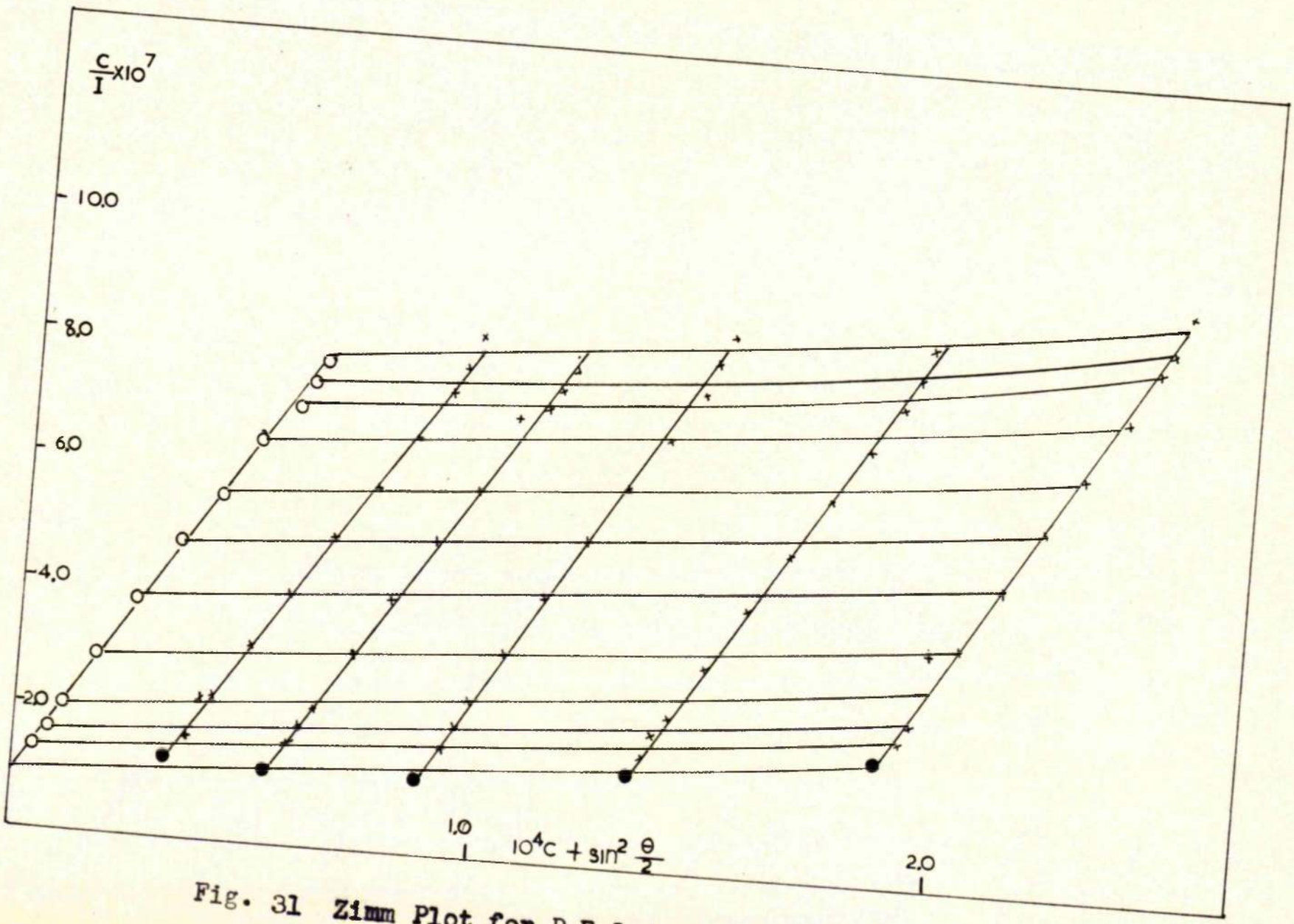


Fig. 31 Zimm Plot for P.E.1 in 0.05 M.KBr

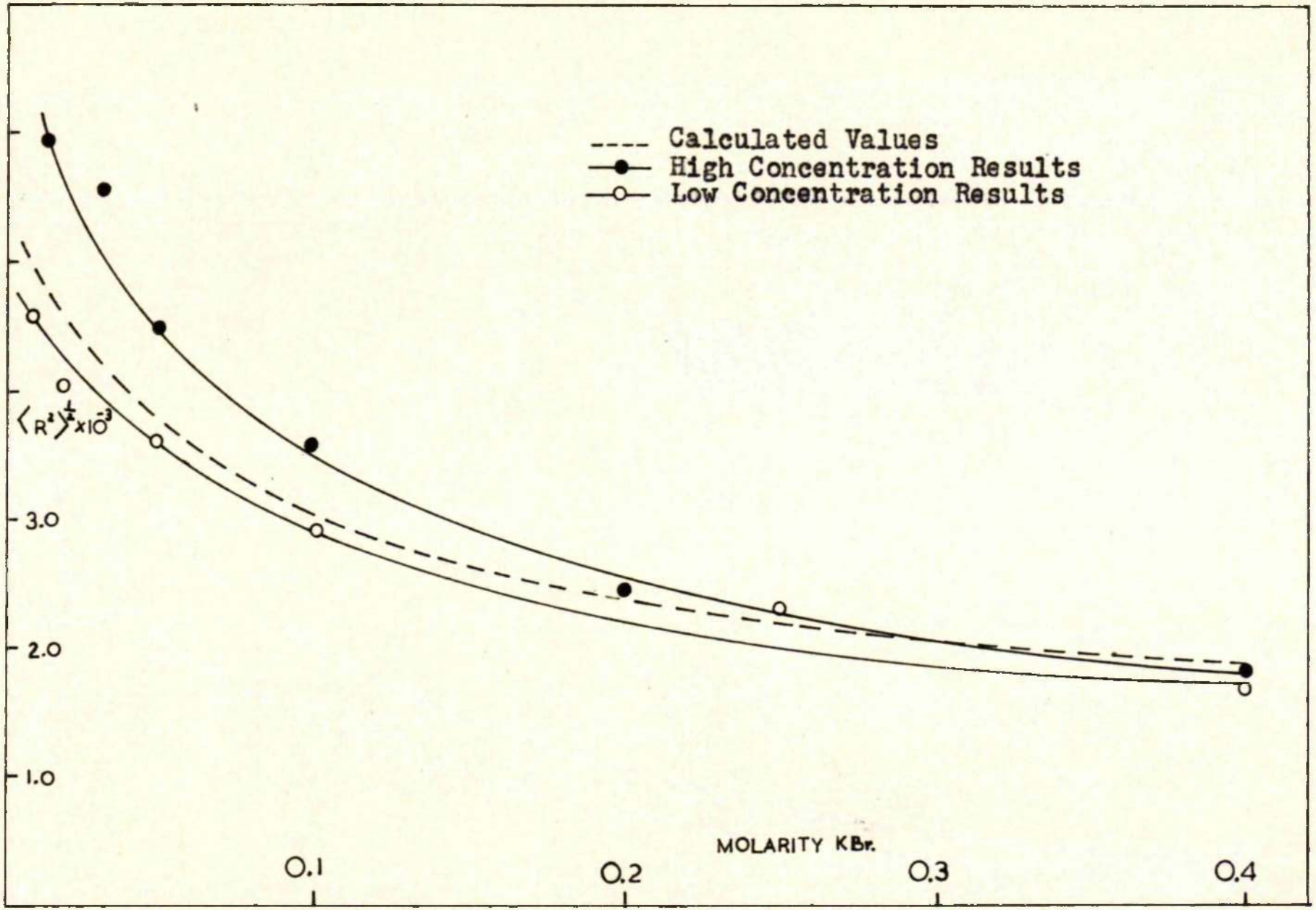


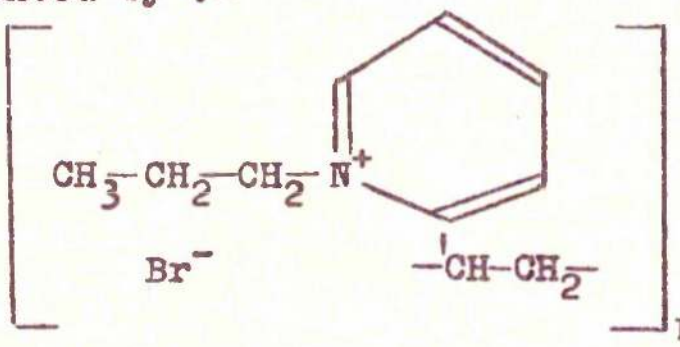
Fig32 Plots of Variation of $\langle R^2 \rangle$ with Molarity of Electrolyte for P.E.1

PART 2.

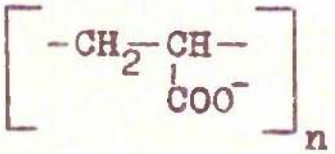
INTRODUCTION.

Polyelectrolytes may be defined as polymeric molecules which contain ionisable groups as part of the structure. Included in this general class are proteins, nucleic acids and synthetic polyelectrolytes.

Synthetic polyelectrolytes may be divided into two types according to the sign of the charge on the macro-ion : cationic and anionic. An example of the former is poly-n-propyl-2-vinyl pyridinium bromide, the structure of which may be represented by :-



This is a strong electrolyte and is ionised at all pH values in contrast to polyacrylic acid which forms a polyion of structure:-



This is a weak polyelectrolyte and the degree of dissociation depends upon the pH of the solution.

Other types of polyelectrolytes include polyampholytes which are copolymers of polyelectrolytes such as the two described above, naturally occurring polymers such as the polyglutamates,and inorganic polyelectrolytes e.g. polyphosphates and polysilicates.

The unique properties of polyelectrolytes include :- solubility in polar solvents, conduction of electricity and long range inter and intra molecular interactions in solution which occur to a much greater extent than in uncharged polymer solutions.

While many methods and techniques have been used to study polyelectrolytes, only viscosity, transport and light-scattering will be reviewed here since viscosity and light-scattering are the main techniques for determining size and shape of large molecules in solution while transport measurements give some indication of the degree of binding of the counterions to the main chain.

Viscosity of Polyelectrolytes.

Measurement of viscosity of polyelectrolytes by Staudinger focussed attention on the unique properties of these molecules in aqueous solution. For a normal non-ionic polymer the reduced viscosity is found to be a linear function of concentration, the line obtained by plotting these quantities having a positive slope. Early measurements[67] on polyelectrolytes, however, revealed a large increase in the reduced viscosity as concentration decreased. It appeared that the line obtained was asymptotic to the reduced viscosity axis which rendered the location of the intercept corresponding to the limiting viscosity number impossible. This effect is very general for polyelectrolytes having been observed for many varied systems e.g. sodium salts of deoxyribonucleic acid[68], polystyrene sulphonate[69], poly-vinyl pyridinium bromide[70] and many others. Early interpretations of this effect included dissociation of aggregates or increased hydration on dilution.

The modern and most satisfactory explanation was proposed in 1948 by several workers[71]. They ascribed the large increase in viscosity to expansion of the polyelectrolyte on dilution.

Fuoss and Strauss[72] showed that the apparently asymptotic behaviour of these plots could be transformed to a linear plot by use of the equation :-

$$\frac{\eta_{sp}}{c} = \frac{A}{1+Bc^{\frac{1}{2}}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (59)$$

The finite intercept obtained may be interpreted as the limiting viscosity number of the polyion in its most extended configuration. The dimensions of molecules calculated from these data have been compared with those determined directly from light-scattering measurements[73].

As the ionic strength of the solution is increased by the addition of simple electrolyte the shape of the reduced viscosity concentration curve tends to that normally obtained for a neutral polymer[74]. When the ionic strength is very high the limiting viscosity number falls below that expected for a neutral polymer of the same chain length and eventually the polyelectrolyte is precipitated. Pals and Hermans[75] showed that if the dilutions of polyelectrolyte were made while keeping the concentration of counterions constant, linear plots of reduced viscosity were obtained. This enabled an estimate of polyion size as a function of salt concentration to be made and the method has been termed "isoionic dilution".

Because of the ease of deformation of large molecules such as the polyelectrolytes it is necessary to extrapolate

all measurements of viscosity to zero rate of shear. A Couette type of viscometer is generally used for liquids showing such non-Newtonian behaviour.

Viscosity Molecular Weight Relationships.

As indicated in Part 1 the value of the exponent a in the Mark-Houwink equation indicates the shape of the particle in solution. Measurements on sodium polymethacrylate yielded a value of $a=2$ indicating a rod-like structure. The results, however, are based on measurements made at finite concentration. As the ionic strength of the solution increasss, lower values of the exponent are obtained. Strauss[76], working on polyphosphates, obtained $a=1.9$ in water and 0.50 in 0.415 M potassium bromide solution showing that the polyphosphate molecule could have a rod-like or random coil configuration depending upon the solvent.

Transport.

Conductance measurements on polyelectrolytes give information concerning the binding of counterions to the polyion chain. Wall[77] et alia have shown that most of the current in solutions of polyacrylic acid is carried by hydrogen ions. This is due to the size of the polyion together with the small charge produced on it. Titration with sodium hydroxide to form a strong electrolyte produced an increase in the proportion of current carried by the polyion[78]. Some of the sodium ions in these experiments were found to move with the polyion to the anode. This indicated that some counterions remain associated with the polyion while some completely escape from its electric field. At high degrees of neutralization the polyion moved at rates comparable to

those of simple ions indicating a large charge coupled with a very extended configuration rendering the molecule almost free draining.

As the dielectric constant of the solvent increases the conductance also increases[79] indicating a decrease in the energy required to remove ions from the chain with a resulting high charge and extended configuration.

The above observations support the view that in polyelectrolyte solutions the counterions are to a greater or lesser extent bound to the polyion. Strauss and co-workers[80] have shown that in solutions of poly-4-vinyl pyridinium bromide the addition of large quantities of simple electrolyte e.g. potassium bromide changes the sign of the charge on the polyion. This effect cannot be ascribed to overall electrostatic attraction since the polyelectrolyte, as a whole, must be neutral but may be interpreted as ion binding at specific sites on the polyelectrolyte due to ion dipole type forces in the molecule.

Light-Scattering by Polyelectrolytes.

Difficulties are encountered when using light-scattering as a method for molecular weight determination for polyelectrolytes since the ionic nature of these molecules modifies the nature of the interactions in the solutions. The effect of the long range electrostatic forces existing in such solutions at low ionic strength is to restrict the degree of randomness of the system and thus to cause an overall decrease in the scatter from it. This effect was first noticed by Guinand[81] who found that the 90° scatter from unionised polyacrylic acid was fifty times that of the

ionised acid. Edsall[82] has modified the multicomponent treatment of Stockmayer to apply to solutions containing ions.

Doty and Steiner[83] observed that the effect of such a non-random system was also to alter the angular dependence of scattered light. They called this effect external interference and showed that for small particles a greater loss occurs in forward than in backward scattering. For large molecules the effect of concentration on dissymmetry of scattered light was illustrated by Oster[84] who showed that in salt free aqueous solutions of tobacco mosaic virus there was a marked decrease in the dissymmetry as concentration increased whereas, in phosphate buffer solution no change in dissymmetry occurred over the same concentration range.

Fuoss and Edelson[85] found that for poly-4-vinyl pyridinium bromide in water, the dissymmetry decreased as concentration decreased, passed through a minimum and, in very dilute solution increased rapidly. With increasing salt concentration the minimum became less pronounced and eventually linear extrapolation to zero concentration was possible. Oth and Doty[86] from measurements on polymeth-acrylic acid in water found that the interactions between molecules increase in parallel with the size of the coil. Stacey[87], working on high molecular weight polymethacrylic acid, showed that in salt solutions normal Zimm Plots could be obtained and that the dissymmetry in water followed the pattern indicated by Fuoss and Edelson.

Other experimental studies on synthetic polyelectro-lytes have been made by Strauss and co-workers[76] on

polyphosphates employing many different techniques. Trap and Hermans[89] in a light-scattering study of polymethacrylic acid found results which are typical of polyelectrolytes including minima in the dissymmetry concentration curve and increasing size of the molecule as the concentration of salt in aqueous solution was decreased. Schneider and Doty,[90] examining a sample of sodium carboxymethylcellulose over a wide range in ionic strength, found that the experimental dimensions calculated were inconsistent with those predicted by theoretical treatments of the expansion of polyelectrolytes as a function of salt concentration. Light-scattering measurements on poly-4-vinyl pyridinium bromide in aqueous salt solutions by Strauss and Williams[91] produced results which indicated that considerable degradation had occurred during the reaction of quaternisation from the parent polymer.

Molecular Weight Determination of Polyelectrolytes.

Most of the determinations of molecular weights of proteins and polyelectrolytes have been made with little regard for the limitations of light-scattering theory. Casassa and Eisenberg[92] have indicated how the multicomponent theory may be applied to solutions of polyelectrolytes containing simple electrolyte. The error involved by the use of the two component theory varies according to the polyelectrolyte-solvent system used. Strauss has shown that a considerable error is incurred for polyphosphates but that it is almost negligible for poly-4-vinyl pyridinium bromide.

Qualitatively the reason for adopting the multi-component theory may be described as follows. When a molecule in solution is surrounded by a binary system, selective

adsorption of one of the components may occur. This is true when both components in the solvent are liquid or when one is a simple electrolyte. The adsorption will alter the polarisibility of the molecule thus affecting the intensity of the scattered light. It has been shown that correct results may be obtained by measuring the refractive index increment at constant chemical potential of simple electrolyte.

If the components 1,2,and3 refer to solvent, poly-electrolyte and simple electrolyte respectively then :-

$$\left(\frac{\partial n}{\partial c_2}\right)_{\mu_3} = \left(\frac{\partial n}{\partial c_2}\right)_{c_3} + \left(\frac{\partial n}{\partial c_3}\right)\left(\frac{\partial c_3}{\partial c_2}\right)_{\mu_3} \qquad \text{.....(60)}$$

Strauss and co-workers[93] have discussed such a system in detail and carried out membrane equilibria studies to determine the quantity $\left(\frac{\partial c_3}{\partial c_2}\right)_{\mu_3}$ directly. For most purposes $\left(\frac{\partial n}{\partial c_2}\right)_{\mu_3}$ can be determined directly using a polyelectrolyte solution which has been dialized against the same concentration of simple electrolyte.

Chain Configuration of Polyelectrolytes.

In an uncharged polymer molecule the forces tending to extend the molecule above the purely random configuration are long range forces. These are forces between remotely connected segments of the same molecule which are in close proximity. In a polyion, the forces between like charges exist over much greater distances and to calculate the

potential energy of the chain a knowledge of electrostatic interactions between all pairs of charges on the chain is required. The theoretical treatment of this problem is difficult and several models have been employed.

Two main types have been treated. The theories of Kuhn, Kunzle and Katchalsky[71], Harris and Rice[94], and Katchalsky and Lifson[95] employ varying types of jointed chain models with the charges distributed at points along the chain. Those of Hermans and Overbeek[71] and Flory[96] assume a spherical model for the molecule with a spherical distribution of charge.

Agreement of the above theories with experimental measurements on the size of polyelectrolytes is at the moment poor. The only agreement between theory and experiment observed has been that obtained by comparing dimensions of sodium carboxymethylcellulose calculated by the theory of Rice and Harris with the experimental values obtained by Doty and Schneider[90].

EXPERIMENTAL.

Two samples were chosen for quaternisation, of molecular weights 2×10^6 and 4.5×10^5. The alkyl halide chosen for the reaction was n-propyl bromide since the boiling point of 71°C was high enough for the reaction to be carried out under normal reflux conditions but low enough for the unreacted material to be removed under vacuum. Previous studies[97,98] on such vinyl pyridines indicated that, while the 4-vinyl compound could be quaternised completely, reaction on the 2-vinyl polymer was incomplete and only some of the nitrogens on the chain were attacked. Because of this, an effort was made to ensure that as much reaction as possible occurred.

10 gms. of polymer were dissolved in ethanol and an excess (20 gms.) of n-propyl bromide was added. The mixture was refluxed for 24 hours. Longer periods were avoided because of the reported degradation of vinyl pyridines in solution. The resulting mixture was poured into an excess of anhydrous dioxane. The solution was decanted, the precipitate dissolved in methanol, and the precipitation process repeated. Residual solvent was removed under vacuum and the product obtained was freeze-dried from a solution in water. This reaction procedure produced polyelectrolyte which was approximately 70% quaternised and freeze drying enabled the material to be obtained in a form convenient for weighing and dissolving.

Attempts were made to carry out the reaction in dimethyl sulphoxide in order to obtain a greater degree of quaternisation. This was not satisfactory due to the

decomposition of dimethyl sulphoxide at temperatures approaching 100°C and to the difficulty of obtaining samples of the product free from solvent. Even after precipitating in ether, all the dimethyl sulphoxide could not be removed and it was impossible to freeze-dry the samples. The analyses of the two polyelectrolytes are shown in table (9).

Properties.

The polyelectrolyte samples used were white in colour and fairly hygroscopic. They were stored in closed bottles and weighings were performed as quickly as possible. Since the dimensions of the polyelectrolyte in various solvents were to be investigated, a preliminary study was made of the solubility. The polyelectrolyte in contrast to the parent polymer, was soluble in only very polar solvents : water, methanol, ethanol, dimethyl formamide and dimethyl sulphoxide. In solvents such as propanol and dioxane the polymer was completely insoluble and, even in ethanol, only dilute solutions could be obtained. This limited the scope of the investigation but, since it has been established[70] that the addition of simple electrolyte to aqueous solutions of polyelectrolytes causes marked changes in the size of these molecules, it was decided that further study of the effect of simple electrolyte on light-scattering from such solutions was warranted. The relatively insoluble nature of the polysalt was again illustrated by its insolubility in solutions of approximately 1 M potassium bromide.

Light-Scattering.

The general techniques described for the parent polymer were again used with some modification. Since solutions of

polyelectrolytes, especially in water, exhibit high viscosity, no attempt was made at filtration and clarification of all solutions was by centrifugation at accelerations 30,000 times that of gravity. While many investigators report great difficulty in removing dust from very polar liquids, this difficulty was to some extent overcome in the technique used in the present study. Identical cleaning methods were used for solvent and solution so that, on subtracting solvent scatter from that of the solution, the scatter due to dust is also allowed for if the dust concentration is similar in both cases. All solutions were inspected under unfiltered mercury light by means of a periscope. Solutions containing any appreciable quantity of dust could be rejected. A further reason against considering the presence of dust in the solutions as a major error was that at low angles, in most investigations, the overall intensity of scatter from the large molecules involved was high.

Refractive Index Increments.

Measurements of this quantity were made on a Brice-Phoenix Differential Refractometer and also on a Hilger-Rayleigh interferometer The results obtained on the different instruments were found to agree very well. interferometer measurements are absolute and do not depend on previous calibration. The quantity measured is the difference in optical path length of the light used on replacing solvent by solution in one half of a divided cell. The ultimate sensitivity of this instrument is very much greater than any other for the determination of Δn, but

control of temperature is important. For volatile solvents, such as methanol, consistent measurements could not be obtained due to evaporation, even when lids were fitted to the cell. For dimethyl sulphoxide absorption of water from the air necessitated rapid readings and some loss in accuracy was inevitable.

Refractive Index Increment at Constant Chemical Potential.

Measurements of refractive index increments at constant chemical potential of bromide ion were made by dializing solutions against the appropriate concentration of salt before measurement. The solution of polyelectrolyte was made up in a standard flask by weight and volume using as solvent a solution of potassium bromide. After complete solution, 5 mls. were transferred to a piece of Visking tubing closed by two knots at one end. The tubing had previously been washed in distilled water to remove any soluble impurities and dried. The open end was sealed in the same manner and the dialysis bag so formed was immersed in a solution of potassium bromide of identical concentration contained in a stoppered flask. The external solution was changed twice during 48 hours. Small amounts of the dialized solution were withdrawn from the dialysis bag by syringe and used for washing the interferometer cell preparatory to making the refractive index increment measurements.

Light-Scattering by Concentrated Polymer Solutions.

In order to explain certain effects noted in the light-scattering behaviour of polyelectrolyte solutions it was necessary to make measurements on the parent polymer at high

concentrations. In order to reach concentrations of 1 - 2% a special technique was used, since the normal method of diluting and centrifuging could not be employed due to the high viscosity of such solutions

250 mls. of solution (concentration 4×10^{-3}) were prepared in the usual way. The solution was centrifuged in eight cells each containing 30 mls. 20 mls. were transferred from each cell after centrifugation to the special light-scattering cell shown in figure (17). The angular scatter from the solution was determined, care being taken to exclude stray light. The weight of the scattering cell had been previously determined. The cell containing the solution was reweighed. Some solvent was removed under vacuum and the cell was closed while still under vacuum. By weighing, the new concentration of solution was found, and another measurement of angular scatter was made. The process was repeated till measurements could no longer be made due to insufficient volume of solution in the cell.

In principle the concentration of the solution obtained after each evaporation could be determined by calculating the weight of polymer in 160 mls. of dilute solution, subtracting the volume of solvent removed from 160 mls. and recalculating the concentration using the new volume. The validity of this when applied to fairly concentrated polymer solutions is doubtful since a volume of solution may be appreciably greater than the volume of solvent having the same weight. An alternative method of measuring the concentration was also applied. 2 mls. of the most concentrated solution were removed by pipette and

transferred to a weighed flask. The polymer remaining on the sides of the pipette was removed by washing with methanol, the washings being added to the flask. Petroleum ether was added to precipitate the polymer and solvent was removed under vacuum. The polymer was redissolved in benzene and the process repeated. The precipitated polymer was dried to constant weight under vacuum and the concentration of the solution calculated.

Dilute Salt Solutions.

While light-scattering runs in fairly high salt concentrations (0.1 to 0.5 M) were made using the appropriate molarity of aqueous potassium bromide as solvent, a more rapid method was used for the addition of very small weights of salt. Five concentrations of polyelectrolyte in water were obtained in the normal way by diluting and centrifuging together with a sample of water similarly treated. After measuring the scatter of each concentration as a function of angle, a very small quantity of concentrated potassium bromide solution, also centrifuged, was added by Agla syringe to each cell. The solution was agitated to ensure mixing of the simple electrolyte and the scattering of each solution was again measured. Several additions of salt were made in this way.

To determine the concentration of simple electrolyte in the solutions, the syringe was calibrated by adding quantities of water, measured in turns of syringe, to a tube and weighing. The process was repeated using the concentrated salt solution. From a knowledge of the density of water the weight of salt added per turn of syringe was calculated. Since the total volume added to each polyelectrolyte

solution was small, it was felt reasonable to neglect changes in the concentration of polyelectrolyte.

Solvents.

Water used in this investigation was deionised by ion-exchange, and had a conductivity less than 5×10^{-6} mhos. Ethanol and dimethyl formamide were used as supplied. Methanol was dried by refluxing over magnesium followed by distillation. Dimethyl sulphoxide was stored over anhydrous calcium sulphate and filtered before use.

RESULTS.

The results of measurements on poly-2-vinyl-n-propyl pyridinium bromide may be divided for ease of representation into three sections :-

1) Light-scattering from solutions of the polyelectrolyte in pure liquids.

2) Light-scattering of the polyelectrolyte in various concentrations of aqueous potassium bromide.

3) Refractive index increments for the polyelectrolyte in salt solutions and in pure liquids.

The light-scattering data are presented in the form of Zimm Plots. This facilitates interpretation of the data and allows the various parameters to be calculated directly.

1) Light-Scattering from Pure Liquids.

In this part of the investigation measurements were made only on the higher molecular weight sample of the two fractions available.

Water :- The polyelectrolyte concentration range employed was 1.25×10^{-4} to 5×10^{-4} gm/ml. The results obtained are shown in figure (18) where only the angles from 25° to 90° are shown.

The solvent when measured for dissymmetry of scattered light gave a value of less than unity. This was traced to reflections from the inside wall of the measuring cell where there was a substantial difference in the refractive indices of glass and solution. This effect was also encountered when working with solutions in methanol and ethanol. The procedure adopted was to minimise the reflections by rotating the scattering cell at each angle. The effect was of greatest

importance when the overall scatter of the solution was low i.e. comparable in magnitude with the reflected light. Since the intensity of scattered light decreased rapidly with increasing angle, the data at high angles are somewhat scattered, and additional measurements were made at low angles - 25°, 33° and 53°.

Because of the unusual light-scattering behaviour of this polyelectrolyte in water, two further runs were made ; one covering a similar concentration range and the other a lower range (2.5×10^{-5} to 1×10^{-4}). In both cases the same type of plot was obtained although the results from low concentrations were erratic due to the very small intensity of scatter. One of the criticisms which may be made of light-scattering measurements in water, is that the results are distorted by the presence of dust. In these experiments the solution appeared dust free when viewed under unfiltered light. The absence of dust is also borne out by the shape of the Zimm Plot and by the general consistency of results obtained from different experiments.

Methanol :- The concentration range covered was 1.25×10^{-4} to 5×10^{-4} gm/ml. No significant differences could be detected between results obtained in unpurified methanol and methanol which had been dried and redistilled. The results are shown in figure (19). These results are not, in general, so consistent as those obtained in water. This is thought to be due to the high volatility of methanol. Some rise in temperature usually occurred during centrifugation and it is possible that this caused changes in concentration. Owing to the difficulty of extrapolating the data, no information on the dimensions of the molecule could be obtained in this solvent.

Ethanol:- A similar concentration range was employed as in water and methanol. The results obtained are shown in figure (20). In this plot, due to the low dissymmetry, somewhat different scales have been employed. The scale of $\sin^2 \frac{\theta}{2}$ has been made much larger than that of concentration. This reverses the position of the $c=0$ and $\theta=0$ lines on the Zimm Plot. Extrapolations are carried out in the same manner as for the more conventional plots and similar data are obtained. As can be seen from figure (20), the lines of constant concentration were distinctly curved at lower angles. This rendered extrapolation more uncertain.

Dimethyl Formamide :- Almost identical concentrations to those above were employed and the Zimm Plot obtained is shown in figure (21). Due to the low intensity of scatter from the solution, coupled with a large solvent scatter, the data obtained in this solvent are poor. Clarification of the solutions was difficult and slight traces of dust could always be observed.

Dimethyl Sulphoxide:- Because of the very low intensity of scatter from solutions with dimethyl sulphoxide as solvent the concentration range employed was 4×10^{-4} to 1.6×10^{-3} gm/ml. As in the case of dimethyl formamide, it was impossible to obtain the solutions free from dust. The Zimm Plot for the polyelectrolyte in this solvent is shown in figure (22).

In view of the difficulties in extrapolating the data in figures (18) – (22), no attempt will be made at present to derive the various molecular parameters such as molecular weight, radius of gyration and second virial coefficient.

Table (10) shows the quantities obtained from the above runs i.e. the intercept $\left(\frac{c}{I}\right)_{c=0,\theta=0}$ and the limiting slopes divided by the intercept of the zero angle and zero concentration lines.

2) Light-Scattering from Potassium Bromide Solutions.

A similar reflection effect to that in pure water was observed in dilute salt solutions. The same procedure was adopted. In general, the results in dilute salt solutions were more consistent than those in pure liquids due to the higher level of light-scattering at the upper angles.

Light-scattering runs were made on the two polyelectrolyte samples (P.E.1 and P.E.2) in several concentrations of salt using a concentration range for the polyelectrolyte of 1.25×10^{-4} to 5×10^{-4}. Examples of the results obtained are shown in figures (23) to (27). Due to the difficulty of extrapolation of some of the data obtained in solutions of low ionic strength, an additional series of runs was made employing approximately half the concentrations used in the first study. The normal methods of evaluating molecular dimensions were applied to these data. Experimental quantities derived are shown in tables (11) and (12).

3) Refractive Index Increment.

a) Pure solvents :- Table (13) shows the values of $\frac{dn}{dc}$ for solutions of the polyelectrolyte in various liquids. There is little variation in this quantity over a considerable range of refractive index. This is unexpected in view of the good agreement obtained with the Gladstone and Dale relationship for the parent polymer in different solvents. The rather poor reproducibility observed for liquids such as

dimethyl sulphoxide and dimethyl formamide is thought to be due to absorption of water from the atmosphere or to temperature variations within the liquid. For methanol, no results could be obtained, since thermal equilibrium was never attained due to surface evaporation.

b) Salt solutions :- Table (14) shows the values of $\frac{dn}{dc}$ for the polyelectrolyte in several molarities of potassium bromide. Values of $\frac{dn}{dc}$ measured for such solutions after dialysis were not significantly different from those measured without dialysis, indicating that the term $\left(\frac{\delta c_3}{\delta c_2}\right)_{\mu_3}$ in equation (60) is zero, within the limits of experimental error.

DISCUSSION.

In this study most of the results have been represented in the form of Zimm Plots since this is the most useful method of observing the effect of concentration and angle on the scattered intensity. In a normal Zimm Plot the lines of constant angle and constant concentration are usually straight. The line indicating $\frac{c}{I}$ as a function of angle may be convex upwards, indicating a departure of the chain configuration from that of a random coil. A high value of polydispersity also produces this effect and it is difficult, in some cases, to separate the two without a knowledge of the polydispersity. An upward curvature of the $\frac{c}{I}$ line for zero angle as a function of concentration is sometimes observed if the concentration range used is sufficiently high for virial terms other than the second to have appreciable values. Owing to the unusual nature of the Zimm Plots obtained in this study the general features will be discussed below.

Light-Scattering from Polyelectrolyte in Pure Liquids.

In water a very large value of dissymmetry was obtained ca. 10. This rendered the extrapolation of the constant concentration lines to zero angle hazardous. Small errors in the location of the zero angle line may lead to considerable error in molecular weight determination due to the small values of the intercept. By plotting the data on a large scale, reasonable precision in the extrapolation was obtained. The slope of the zero angle line as a function of concentration was very small. This is unexpected. Other workers[90,91] have found B to increase markedly with decreasing salt concentration. The line showing $\frac{c}{I}$ as a

function of angle at zero concentration has a double curvature being first concave upwards at low angles and concave downwards at high angles. This is in agreement with the shape of the line corresponding to the full expression for $P^{-1}(\theta)$ for a chain molecule exhibiting excluded volume. The most significant fact which is clearly shown in the plot is that the lines of constant angle converge towards zero concentration. That this fact is not unique to water is shown by figure (19) for methanol. The same marked increase of the angular dependence of scattered light with concentration is observed. In this case no meaningful extrapolation of the constant angle data to zero concentration could be made, since the lines of constant angle seemed to intersect, and no estimate of the size of the molecule could be obtained. The intercept $\left(\frac{c}{I}\right)_{c=0,\theta=0}$ in methanol was higher than that obtained in water by a factor of seven while the value of $\left(\frac{c}{I}\right)_{\theta=0,}$ did not appear to change appreciably over the concentration range studied indicating a zero second virial coefficient.

In dimethyl sulphoxide and dimethyl formamide similar effects were observed. The angular dependence of scattered light changed considerably with concentration and the intercepts obtained in both of these solvents were much larger than those obtained in methanol and water. Due to the sharp curvature of the constant concentration lines, extrapolation to zero angle was difficult. As seen from figure (22) the lines of zero concentration and zero angle both appear to have zero slopes for dimethyl sulphoxide. In figure (21), however, positive values for the slopes of both of these lines were obtained for dimethyl formamide.

Figure (20), representing the light-scattering behaviour observed with ethanol as solvent, may be divided into two parts. Data at high angles (75° - 135°) produced a normal type of Zimm Plot which would indicate a small particle i.e. less than 200 A°, and a large value of second virial coefficient. In this high angle region linear extrapolation to zero angle and zero concentration is possible. At lower angles, however, there is distinct curvature of the lines of constant concentration as a function of angle. This curvature is most evident at the higher concentrations and decreases with concentration so that, in the limit of zero concentration, linear extrapolation of $\frac{c}{I}$ to zero angle is possible. Even if extrapolations at constant concentration are made to include the curvature at lower angles, a finite value for the second virial coefficient is obtained.

The observations described above may be summarised as follows :-

1. There is a hundred-fold increase in the value of the intercept $\left(\frac{c}{I}\right)_{\theta=0,c=0}$ on going from water to dimethyl sulphoxide as solvent.

2. In all solvents there is a large variation in the angular distribution of scattered light with concentration which, in most cases, renders extrapolation to zero concentration uncertain so that the application of normal light-scattering formulae for obtaining molecular dimensions is impossible.

3. There is no systematic change of the second virial coefficient with solvent as is usually encountered with neutral polymers.

Light-Scattering from Polyelectrolyte in Salt Solutions.

The reasons for making a complete investigation of the effect of ionic strength on the light-scattering from such a polyelectrolyte were :-

1. The unique effects met with in pure solvents indicated that such measurements cannot be interpreted as simply as can measurements on unionisable polymers.
2. Although some measurements have been reported on the expansion of polyelectrolyte molecules as a function of ionic strength, most of these have been based on dissymmetry measurements and few have dealt with the complete reciprocal intensity scattering envelope.
3. It is known that the addition of simple electrolyte to solutions of polyelectrolyte tends to make the viscosity behaviour approach that of a neutralpolymer. It is of interest, therefore, to observe any similar changes in light-scattering behaviour as a function of ionic strength.

From figures (23) to (25) a consistent change in the general shape of the Zimm Plot is apparent. In very dilute solution, figure (23), the plot is similar to that obtained for water. As the salt concentration increases, the dissymmetry becomes smaller, as would be expected from current theories, but also the convergence of lines of constant angle towards zero concentration becomes less pronounced, and at high concentration of salt, almost normal types of Zimm Plots are obtained. In figure (25) the constant angle lines are parallel and any slight curvature on the zero concentration line as a function of angle may be interpreted

as evidence of the excluded volume of the coil.

In addition to the change in the shape of the Zimm Plots and decrease of apparent molecular dimensions with increasing ionic strength, a distinct variation of the intercept is evident in table (11). This variation is greater than the experimental error for such measurements. For the high molecular weight sample a range of 2.5 in intercept is observed while for the low P.E.2 a range of 3 is covered.

The measurements on the slope giving the second virial coefficient are difficult to interpret because of the smallness of this quantity. It seems certain however that the very large changes observed by other workers[90] are not being observed. In the case of P.E.2 at fairly high concentrations of salt (0.5 to 0.25 M) negative slopes were obtained for the $\left(\frac{c}{I}\right)_{\theta=0}$ against concentration line. A similar effect was not observed for the higher molecular weight sample.

It was evident from the results obtained in the above part of the investigation that normal light-scattering behaviour was not being observed in solutions of polyelectrolytes except in solutions containing large concentrations of potassium bromide. One explanation was that, due to the ionic nature of the polyelectrolyte, long range coulombic interactions were operative and that a diminution of scattering was being caused by the resulting decrease in randomness of the system. Other investigators, encountering such effects, have noted an increase in dissymmetry with decrease in concentration e.g. Oster on tobacco mosaic virus.[84] A theoretical treatment of the problem by Albrecht[99], who

considered double contacts existing between neutral polymer molecules in solution, resulted in an equation of the form :-

$$\frac{Kc}{R_\theta} = \frac{1}{MP(\theta)} + 2Q(\theta)Bc \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(61)$$

for the more usual Debye Equation. The function $Q(\theta)$ describes the variation in the angular dependence of scattered light with concentration. Albrecht quotes, as experimental evidence of this effect, the results of Schultz[100] on poly-vinyl acetate. Similar examples exist in the literature e.g. results of Hyde and Wippler[101] on poly-styrene in benzene. These results differ from those obtained in the present investigation, however, inasmuch as the function $Q(\theta)$ predicts a decrease in the dissymmetry as concentration increases while quite the reverse is true in the present study.

Light-Scattering from Concentrated Polymer Solutions.

Calculation of the total volume of molecules per c.c. at the concentration of polyelectrolyte measured in water, using the radius of gyration obtained by light-scattering, revealed that there was considerable interpenetration of molecules. Because of this it was thought useful to examine the light-scattering of the parent polymer in more detail especially in regions of high concentrations where similar interpenetration of molecules would occur. Fraction 1, of molecular weight 4.5×10^6, was used.

The investigation was carried out in two parts. The first was conducted by successively diluting a concentrated

solution. The second involved use of the special cell described above. These procedures enabled a concentration range from 1×10^{-4} to 1.5×10^{-2} gm/ml. to be covered. Figure (28) shows the complete reciprocal intensity scattering envelope over this concentration range. It is composed of three separate sets of results obtained from three distinct runs each covering a separate concentration range : $1 \times 10^{-4} - 4 \times 10^{-4}$, $1 \times 10^{-3} - 4 \times 10^{-3}$ and $4 \times 10^{-3} - 1.5 \times 10^{-2}$ gm/ml. These results are seen to be quite superimposable, and facilitate understanding of the light-scattering from dilute polyelectrolyte solutions.

Figure (28) may be divided into three sections :-

1. At very low concentrations of polymer $1 \times 10^{-4} - 4 \times 10^{-4}$ gm/ml. the shape is that of a normal Zimm Plot. Linear extrapolations are possible to infinite dilution and, because of the small concentration range, no curvature of the lines is observable.

2. At concentrations up to approximately 4×10^{-3} gm/ml. a convergence of constant angle lines as a function of concentration is seen. This region corresponds to that in which the effect predicted by Albrecht is observed. Over this range of concentration the line $\left(\frac{c}{I}\right)_{\theta=0}$ has a distinct upward curvature indicating a positive value for the third virial coefficient.

3. In the high concentration region above 4×10^{-3} the lines of constant angle begin to diverge. The dissymmetry of scattered light increases with concentration. This effect is very similar to that encountered in the polyelectrolyte measurements. In the case of the uncharged polymer this

behaviour can only be ascribed to the effect of large interactions existing between molecules on the light-scattering of the solution. It is possible, although the effect is met with in polyelectrolyte solutions at concentrations very much lower than in uncharged polymer, that this is due merely to the very much larger distances over which the electrical forces existing in polyelectrolyte solutions may act. In contrast to the upward curvature of the $\left(\frac{c}{I}\right)_{\theta=0}$ line at lower regions of concentration, this line at high concentration shows a decrease of slope. This indicates a negative value of the fourth or higher virial coefficients.

As is obvious from figure (28), extrapolation to zero concentration of data obtained in too high a region of concentration, may result in a value for the intercept which is larger or smaller than the true one and that the slopes of lines obtained from $\frac{c}{I}$ against c at a given angle may bear no relation to the slope giving the value of the second virial coefficient. This indicates that the extrapolations made from data obtained with pure liquids as solvents may not be valid and that reliable results as to molecular weights and dimensions may be obtained, for the polyelectrolyte, only in fairly high salt concentration.

A further interesting point which may be observed from this study of concentrated polymer solutions is that, if the dissymmetry of scattered light is plotted as a function of concentration as shown in figure (29), the shape of the curve obtained is very similar to that obtained by Fuoss and Edelson[85] for poly-4-vinyl pyridinium bromide in water.

Determination of Molecular Weights.

Since one of the main uses of light-scattering techniques is in the determination of molecular weights of polymeric molecules including many products of biological importance, it is useful to compare the results of molecular weights estimated by light-scattering with those expected from analysis data on the polyelectrolyte together with a knowledge of the molecular weight of the parent polymer.

Calculation of Molecular Weights from Analysis.

P.E.1. Molecular weight of parent polymer = 2.14×10^6.

Since analysis indicates 68% quaternisation the formula may be written as $\left(C_7H_7N + 0.68\ C_3H_7Br \right)_n$ where n is the degree of polymerisation.

Assuming no degradation during the quaternisation reaction

$$n = 1.94 \times 10^4$$

$\therefore$ Molecular weight of P.E.1 = 3.66×10^6

Applying the same procedure to P.E.2 which is 73.6% quaternised, a molecular weight of 8.39×10^5 is obtained.

Pure Liquids.

The wide variation in intercept of 1×10^{-7} to 115×10^{-7} obtained in different solvents for P.E.1 indicates that for molecular weight determination in these solvents to be consistent, the value of $\frac{dn}{dc}$ must also vary considerably. While by the Gladstone and Dale relationship for the variation of $\frac{dn}{dc}$ with refractive index of solvent,

a smaller value of $\frac{dn}{dc}$ would be expected in dimethyl sulphoxide than in water, no apparent change in $\frac{dn}{dc}$ with solvent is observed. If the normal procedure for molecular weight determination is applied a different molecular weight for the same polyelectrolyte is obtained in each solvent. These values range from 4.7×10^6 in water to 4.7×10^4 in dimethyl sulphoxide. Two qualitative explanations may be advanced for the very low molecular weights obtained in all solvents other than water.

1. When the polyelectrolyte is dissolved in a solvent a proportion of the bromide ions is dissociated. These bromide ions will contribute to the scatter so that the quantity being measured is the molecular weight of a heterogeneous mixture of polyions and simple bromide ions. This is considered unlikely since it has been shown that simple ions only scatter independently when the concentration is less than 10^{-4}M.[102]. Also, this explanation would not account for the high value of molecular weight obtained in water.

2. Due to the dissociation of bromide ions from the polyelectrolyte, coulombic interactions develop in the solution and, because they are operative over considerable distances, impose some degree of order on the system reducing the fluctuations and thus the intensity of scattered light.

This is felt to be the most likely explanation when the result of the study on concentrated solutions is borne in mind. The effect of the total intensity of scatter being reduced is evident in all solvents except water. In this solvent, where ionisation would be expected to be most complete, the high intensity of scatter at low angles is

attributed to the additional effects of such interactions, namely those of increasing the angular dependence of $\frac{c}{I}$ and producing negative values for the higher virial terms.

Molecular Weights in Dilute Salt Solutions.

As seen from table (11) the intercepts obtained in dilute salt solutions change appreciably with concentration of simple electrolyte for both of the polyelectrolyte samples studied. With decrease in salt concentration smaller values of the intercept are obtained. While this change is not so marked as that observed in systems employing pure liquids as solvents, some doubt is present as to the true molecular weights of the polyelectrolytes.

The values of $\frac{dn}{dc}$ employed in the calculation of molecular weights was 0.203, independent of salt concentration, since the careful study made on refractive index increments indicated no change either with external salt concentration or after dialysis. This latter point confirms the observations of Strauss et alia[91] who found very small values for the term $\left(\frac{\partial c_3}{\partial c_2}\right)_{\mu_3}$ in equation (60) when working on the isomer of this polyelectrolyte.

The range of molecular weights shown in table (11) is seen to tend to a limiting value at high salt concentration. Since the addition of simple electrolyte is known to reduce ionisation, the smaller values of molecular weight will approximate more closely to the true ones. The limiting values of molecular weights calculated are 2.02×10^6 for P.E.1 and 6.3×10^5 for P.E.2. Both of these values are

below those calculated from the analyses. This is understandable since it is very likely that some degradation of the polymer or polyelectrolyte occurred during the quaternisation reaction. Much greater degradation has been reported[91] during the quaternisation of poly-4-vinyl pyridine and it is known from qualitative measurements made on poly-2-vinyl pyridine at temperatures ca. 100°C that considerable degradation occurred. Such degradation should be observable as increased curvature of the $P^{-1}(\theta)$ line on the Zimm Plot. As seen from figures (25) and (27), these lines are curved, but calculations to determine the polydispersity are likely to be unreliable due to the large excluded volume effect for such highly extended molecules.

In the very comprehensive investigation of sodium carboxymethylcellulose by Doty and Schneider, where light-scattering measurements were made in four salt concentrations covering a range in molarity of 0.5 to 0.005, there seems to be a parallel increase in molecular weight with decreasing salt concentration although on a much smaller scale than is apparent in this study. The molecular weight range obtained is from 4.8×10^5 to 3.8×10^5 which seems to lie outside that normally obtained in such measurements, particularly as a single value of refractive index increment was employed.

While in principle it is possible to obtain accurate molecular weights of polyelectrolytes by light-scattering on addition of simple electrolyte to the solution, in the light of the above results, it would seem that such molecular weights may not be completely reliable unless it can be shown that the value of molecular weight obtained does not

vary over a considerable range in concentration of added salt.

Molecular Dimensions in Salt Solutions.

While the presence of considerable interaction forces in the polyelectrolyte solutions and their effect on the angular distribution of scattered light may cast some doubt on the validity of the extrapolations it is felt that in the more concentrated salt solutions correct values of the molecular dimensions are obtained.

The values of $\langle R^2 \rangle$ quoted in table (11) were calculated on the basis that the molecule behaves as a random coil. This may be criticised on two counts :-

1. Rod-like structures have been reported for some polyelectrolytes in solution.

2. The relationship existing between the directly measured radius of gyration and the mean square end to end distance of the polyelectrolyte chain is not given by the relationship :-

$$\langle R^2 \rangle = 6\langle \rho^2 \rangle$$

The idea that the polyelectrolyte under discussion exists as rod-like molecules in solution is discounted since the contour length of the chain is 25,600 A° which is more than three times the value of $\langle R^2 \rangle^{\frac{1}{2}}$ obtained in water for P.E.1.

The second criticism is more valid since departure of the polyelectrolyte chain from the truly random configuration is almost certain. Present day theories of polyion expansion, however, are somewhat approximate and it is felt

that the dimensions obtained by making the above assumption are sufficiently precise to test any of the current theories.

The theories, which attempt to predict quantitatively the variation in size of polyelectrolytes as a function of ionic strength, do so by evaluating the electrostatic forces tending to expand the molecule above the size which it would have in an uncharged condition. This is true whether a chain or sphere model is used. A fundamental difficulty inherent in any study is the evaluation of the size of such a molecule in this uncharged condition. Two different criteria are applied. In the early theory of Hermans and Overbeek[71] this uncharged state corresponded to the size obtained by extrapolating molecular dimensions measured at different values of ionic strength to infinite ionic strength. Doty and Schneider applied this method in their study of sodium carboxymethylcellulose. The dimensions of this molecule at infinite ionic strength agreed with those of the uncharged polymer cellulose. In other studies, when this has been attempted,[76] a negative value for the dimensions at infinite ionic strength has been obtained. Such an extrapolation is shown in figure (30) from the results obtained in the present investigation. For compounds such as poly-vinyl pyridinium salts and polyphosphates which can be salted out of solution an alternative procedure may be adopted. This procedure is due to Flory[96] who suggests that a Θ-solvent may be defined for a polyelectrolyte in a manner similar to that for an uncharged polymer. The composition of the Θ-solvent is a molarity of salt such as to make the second virial coefficient zero.

For the purposes of examining the expansion of poly-2-vinyl-n-propyl pyridinium bromide quantitatively as a function of ionic strength, the molarity of potassium bromide corresponding to the θ solvent is taken as 0.4 M. for the high molecular weight sample. This is felt to be justified since the value of $\langle R^2 \rangle^{\frac{1}{2}}$ in this solvent (1.73×10^3 A°) is close to that obtained for the true unperturbed dimensions of the parent polymer (1.5×10^3). The smaller degree of polymerisation of the polyelectrolyte due to degradation will be countered to some extent by the increased hindrance to rotation due to the inclusion of propyl groups in the chain. Also, while no large variations in second virial coefficient were observed for P.E. 1, the value of the slope of all constant angle lines in 0.4 M. salt was essentially zero.

Of the available theories which predict polyelectrolyte expansion, most give much higher values than those observed in experimental studies. That of Hermans and Overbeek predicts an expansion eight times that observed for sodium carboxymethylcellulose while Flory's theory gives a thirty-fold difference. The most fruitful theory is that of Rice and Harris[94] which gives fairly good agreement with the experimental results on the above polyelectrolyte. It is interesting to attempt a comparison between values of dimensions calculated from the Rice and Harris theory with those obtained by experiment for a vinyl type polyelectrolyte since this is quite different in character from the cellulose type which, even in the uncharged state, has a much more extended configuration due to chain stiffness.

Solutions of Low Polyelectrolyte Concentration.

In the above discussion of light-scattering in dilute salt solutions, attention has been focussed on results obtained from a polyelectrolyte concentration range from 1.25 - 5 x 10^{-4} gm/ml. The additional series of measurements made at lower polyelectrolyte concentration (0.5 - 2 x 10^{-4} gm/ml.) corroborates the main points outlined above. The Zimm Plots obtained in this part of the investigation were linear from high salt concentrations to much lower values of ionic strength than in the higher polyelectrolyte concentration range. Figure (31) shows the Zimm Plot obtained for P.E.1 in 0.05 M. potassium bromide in this low polyelectrolyte concentration range. The behaviour is seen to be more normal than in figure (24). At very low values of ionic strength the same unusual behaviour is observed as described above.

The results of this investigation (table 12) have been kept separate and agreement of the data from the two concentration ranges with the predicted values should furnish additional evidence as to the validity of light-scattering measurements of polyelectrolyte dimensions. In general the values of $\langle R^2 \rangle^{\frac{1}{2}}$ are smaller in table (12) than in table (11) and, though the same trend in molecular weight is observed, the intercepts shown in table (12) are somewhat smaller than those in table (11).

Rice and Harris Theory of Polyelectrolyte Expansion.

The model for a polyelectrolyte on which this theory is based is a freely jointed chain of N statistical elements

each of length A. This is essentially the Kuhn model for a polymer chain in which statistical elements comprise enough individual bonds for the orientation of any element to be independent of that of the preceding element in the absence of electrostatic charges but are numerous enough for the configuration of the chain as a whole to be gaussian.

Any chain may be divided into such statistical elements by solution of the equations :-

$$\langle R_o^2 \rangle = NA^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (62)$$

$$L = NA \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (63)$$

where $\langle R_o^2 \rangle$ is the mean square end to end distance of the molecule in the hypothetically uncharged condition and L is the contour length of the chain. In the simplified form of the theory which will be applied here, a further modification of the model is necessary. Since the distribution of charges along any particular element is not known, an even spacing of charges is assumed so that the nett charge on any one element may be concentrated at the centre of the element. Z is the nett number of charges on one element. Due to mathematical complexity, only interactions between charges on neighbouring elements are considered.

The effect of charges on neighbouring segments is to increase the average value of $\cos\gamma$ where γ is the supplement of the angle between any two elements. It has been shown that[103]

$$\langle R^2 \rangle = \langle R_o^2 \rangle \frac{1+\overline{\cos\gamma}}{1-\overline{\cos\gamma}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (64)$$

where $\overline{\cos\gamma}$ is the average value of $\cos\gamma$. Rice and Harris have evaluated $\overline{\cos\gamma}$ as :-

$$\overline{\cos\gamma} = \frac{\int \cos\gamma \exp.\left(-u(\gamma)/kT\right) d\Omega}{\int \exp.\left(-u(\gamma)/kT\right) d\Omega} \quad \ldots\ldots\ldots(65)$$

where $u(\gamma)$ is the potential energy of interaction between charges on adjacent elements. The above integrals extend over all possible orientations and $d\Omega$ is the element of solid angle through which rotation of the statistical element may occur. k is Boltzmann's Constant and T the Absolute temperature.

For the simplified model where the charge is located at the centre of each element :-

$$u(\gamma) = \frac{Z^2\varepsilon^2 \exp.\left(-\kappa r_{ij}(\gamma)\right)}{Dr_{ij}(\gamma)} \quad \ldots\ldots\ldots\ldots(66)$$

ε is the electronic charge and D the dielectric constant of the solution. The quantity $r_{ij}(\gamma)$ is the distance between the charges i and j when the angle between the elements is γ

$$r_{ij}(\gamma) = A \cos\frac{\gamma}{2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(67)$$

κ is the reciprocal of screening constant and is the Debye length given by :-

$$\kappa^2 = \frac{4\pi\varepsilon^2}{DkTV} \sum n_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(68)$$

where V is the volume of a polymer molecule and n_i is the number of ions of type i in the solution per polyelectrolyte molecule. An alternative method[104] for the calculation of κ is :-

$$\frac{1}{\kappa} = \frac{3.041 \times 10^{-8}}{c^{\frac{1}{2}}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (69)$$

where c is the concentration of univalent electrolyte in the solution in moles per litre.

The values of $\overline{\cos\gamma}$ were calculated for P.E.1 in three concentrations of salt solution ranging from 0.2 M to 0.01 M.

The procedure for the evaluation of N and A was as follows :-

Equations (62) and (63) were solved for N and A using a value of 2×10^6 A^{o2} for $\langle R_o^2 \rangle_w$. The contour length of the chain, L, was found from the relation :-

$$L = 2Dp1\left(\frac{2}{3}\right)^{\frac{1}{2}}$$

where Dp is the degree of polymerisation, 1 is the carbon-carbon bond length and the last term accounts for the effect of valence angle. L was found to be 27,500 A^o and the values of N and A are 352 and 78.2 A^o respectively. These are independent of salt concentration.

For each salt concentration the value of $\overline{\cos\gamma}$ was determined in the following way :-
κ was evaluated from equation (69). For 17 values of γ ranging from 10^o to 170^o values of $r_{ij}(\gamma)$ were calculated using equation (67). $u(\gamma)$ was also evaluated for each angle

using equation (66). Z, the number of charges, was evaluated as 21 per element, ε the electronic charge was taken as 4.8×10^{-10} e.s.u. and D, the dielectric constant, as 80. The expression $\exp.\left(-u(\gamma)/kT\right)$ was calculated at each angle with $k = 1.38 \times 10^{-16}$ and T = 300. $d\Omega$ is given by the formula

$$d\Omega = 2\pi \sin\gamma \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (70)$$

$d\gamma$ being constant at 0.1746 radians. The expressions to be integrated were calculated for each angle, using the appropriate value for $d\Omega$, and summed. The value of $\overline{\cos\gamma}$ was found by dividing the sums obtained for the numerator and denominator in equation (65). Equation (64) was used to calculate the value of $\langle R^2 \rangle_w$.

The results of this calculation in three different salt concentrations are shown below.

Molarity KBr	$\langle R^2 \rangle_w$	$\langle R^2 \rangle_z$
0.2	5.2	7.8
0.1	6.0	9.0
0.01	18.5	27.7

These results correspond to the dotted line in figure (32). The filled circles represent the data obtained in the higher concentration range and the open circles the data from the lower polyelectrolyte concentration range. The two sets are seen to agree fairly well from 0.4 M. to 0.2 M. salt. Below this molarity larger values than theoretical were obtained in the higher polyelectrolyte

concentration range indicating that the very large values of dissymmetry measured at low ionic strength were due in part to intermolecular ionic forces in the solution. Data obtained from the lower concentrations of polyelectrolyte agree very well with the calculated values of the dimensions over the salt concentration range 0.4 to 0.01 M.

TABLE 9. Analyses of Polyelectrolytes.

	% H	% C	% N	% Br
P.E.1	5.79	61.56	9.67	23.3
P.E.2	5.81	59.75	9.51	25.3

TABLE 10. Results from Zimm Plots in Pure Liquids.

Solvent	Intercept x 10^7	$\left(\frac{\text{Slope}}{\text{Int.}}\right)_{c=0}$	$\left(\frac{\text{Slope}}{\text{Int.}}\right)_{\theta=0}$
Water	1	30	–
Methanol	7	–	–
Ethanol	12	0.8	8.8×10^{-3}
Dimethyl-formamide	34	1.8	7.5×10^{-5}
Dimethyl-sulphoxide	115	–	–

TABLE 11. Results from Zimm Plots in Salt Solutions.

Polyelectrolyte Concentration Range 1.25 - 5 x 10^{-4} gm/ml.

Salt Conc. Molarity	Intercept x 10^{7}	$\left(\frac{\text{Slope}}{\text{Int.}}\right)_{c=0}$	$\left(\frac{\text{Slope}}{\text{Int.}}\right)_{\theta=0}$	M_w x10^{-6}	$\langle R^2\rangle_z^{\frac{1}{2}}$ x10^{-3}
P.E.1.					
0	1.0	30.2	0	4.8	7.7
1.25 x 10^{-3}	1.0	27.5	0	4.8	7.3
3.75 x 10^{-3}	1.0	25.8	0	4.8	7.0
7.50 x 10^{-3}	1.0	21.0	0	4.8	6.3
1.37 x 10^{-2}	1.0	18.6	6 x 10^{-5}	4.8	5.95
2.62 x 10^{-2}	1.0	16.4	0	4.8	5.60
5.00 x 10^{-2}	1.3	10.6	9 x 10^{-5}	3.7	4.5
0.10	1.55	6.83	0	3.1	3.6
0.20	1.86	3.06	0	2.58	2.4
0.40	2.36	1.58	0	2.02	1.7
P.E.2.					
0	2.0	29	0	2.4	7.42
1.47 x 10^{-3}	2.0	24	0	2.4	6.75
7.50 x 10^{-3}	2.0	12.3	0	2.4	4.84
1.03 x 10^{-2}	2.0	13.7	0	2.4	5.11
2.50 x 10^{-2}	2.0	10.7	0	2.4	4.50
0.1	4.1	3.9	0	1.17	2.60
0.25	5.8	1.7	-1.6x10^{-4}	0.83	1.80
0.5	7.6	0.4	-6.6x10^{-4}	0.63	0.87

TABLE 12. Results from Zimm Plots in Salt Solutions.

Polyelectrolyte Concentration Range 0.5 - 2 x 10^{-4} gm/ml.

Salt Conc. Molarity	Intercept x 10^{7}	$\left(\frac{\text{Slope}}{\text{Int.}}\right)_{c=0}$	$\left(\frac{\text{Slope}}{\text{Int.}}\right)_{\theta=0}$	M_w x10^{-6}	$\langle R^2 \rangle_z^{\frac{1}{2}}$ x10^{-3}
P.E.1.					
2.0 x 10^{-3}	1.2	32.5	0	4.0	7.91
4.0 x 10^{-3}	1.2	22.2	0	4.0	6.53
1.0 x 10^{-2}	1.8	11.1	0	2.65	4.60
2.0 x 10^{-2}	1.8	8.5	0	2.65	4.04
5.0 x 10^{-2}	1.5	7.3	0	3.17	3.74
0.1	1.8	4.4	2 x 10^{-3}	2.65	2.92
0.25	1.5	3.0	1.6x10^{-3}	3.17	2.40
0.40	1.7	1.6	0	2.80	1.75
P.E.2.					
1.2 x 10^{-3}	4.8	12.3	0	1.0	4.86
2.4 x 10^{-3}	6.0	5.5	0	0.8	3.24
6.0 x 10^{-3}	5.1	5.5	0	0.93	3.24
1.2 x 10^{-2}	4.6	3.4	0	1.03	2.55
3.0 x 10^{-2}	6.0	2.4	0	0.8	2.14
6.0 x 10^{-2}	6.6	1.3	0	0.72	1.56
0.1	6.9	1.0	0	0.68	1.40
0.15	6.3	1.2	1.8x10^{-3}	0.75	1.55
0.30	6.3	0.84	1.0x10^{-3}	0.75	1.27
0.5	6.0	0.66	0.9x10^{-3}	0.80	1.13

TABLE 13. Refractive Index Increment in Pure Liquids.

Liquid	$\frac{dn}{dc}$ (Av.)
Water	0.204
Methanol	–
Ethanol	0.201
Dimethyl-formamide	0.210
Dimethyl-sulphoxide	0.197

TABLE 14. Refractive Index Increment in Salt Solutions.

Molarity KBr	$\left(\frac{dn}{dc}\right)_{c_3}$	$\left(\frac{dn}{dc}\right)_{\mu_3}$
0.01	0.204	0.206
0.1	0.202	0.200
0.2	0.205	0.210
0.4	0.199	–
0.5	0.203	0.198

CONCLUSIONS.

1. Although the quaternisation reaction between poly-2-vinyl pyridine and n-propyl bromide did not go to completion, enough reaction occurred to render the product a strong polyelectrolyte.

2. Some degradation occurred during the reaction to quaternise the polymer.

3. "Normal" light-scattering behaviour is observed for this polyelectrolyte only in solutions of moderately high ionic strength.

4. In other solutions of salt, an apparent increase in molecular weight was obtained with increased scatter at low angles.

5. In liquids other than water, a general decrease in scatter was observed, resulting in apparent molecular weights which were small compared to those calculated from analysis data.

6. The cause of (5) and (4) is thought to be due to inter-molecular forces acting over large distances in the solution due to the ionic nature of the polyelectrolyte which considerably modify light-scattering behaviour.

7. This explanation of the effects met with in dilute solutions of polyelectrolyte is substantiated by the study in concentrated polymer solutions which exhibit similar behaviour at high concentrations.

8. The Rice and Harris Theory of polyelectrolyte expansion

predicts the variation of the molecular dimensions of this polymer very well over the range of ionic strength 0.4 to 0.01.

9. The main conclusion which may be drawn from the present investigation is that care must be taken in the interpretation of data obtained by light-scattering from high molecular weight charged polymers. The ionic interactions, which are operative even in solutions of very low concnetration, may lead to very inaccurate values for molecular weights and dimensions. It is suggested that in salt solutions the angular distribution of scattered light can be taken as a function of the dimensions of the molecule only when the ratio, in terms of normality, of simple electrolyte to polyelectrolyte is high. This sets a lower limit on the range in ionic strength over which polyelectrolyte dimensions may be studied since the overall scatter of the solution will decrease with the polyelectrolyte concentration.

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